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# NOTES ON LEAD AND CADMIUM FERROCYANIDES.

BY EDMUND H. MILLER AND HENRY FISHER.

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## LEAD FERROCYANIDE.

THE following series of experiments were made in order to ascertain whether the composition of lead ferrocyanide is invariably $Pb_2Fe(CN)_6$, or whether, like the ferrocyanides of manganese and zinc, it is affected by the conditions of precipitation.

The precipitates were made as follows: Lead acetate was dissolved in water and heated to boiling, to this a hot aqueous solution of potassium ferrocyanide was added, and acid in some cases as is noted later. The precipitates were allowed to settle and were washed by decantation until free from lead or ferrocyanide as indicated by hydrogen sulphide, or by ferric chloride. They were then dried at 105° C. to constant weight. The method of analysis was in all cases as follows: About one gram was dissolved in dilute nitric acid in a casserole, and after the addition of sulphuric acid, evaporated to fumes. One evaporation was found to effect complete decomposition. The residue was taken

up with 1 per cent. sulphuric acid to which half its volume of alcohol was added. The lead sulphate was washed with 1 per cent. sulphuric acid containing alcohol, filtered and weighed in a Gooch crucible. The iron was precipitated in the filtrate by ammonia, after boiling out the alcohol and adding ammonium chloride, filtered, washed, and weighed as $Fe_2O_3$. The filtrate from the iron was evaporated to dryness in platinum, the ammonia salts volatilized and the potassium sulphate weighed.

A. Precipitate formed in a neutral solution with lead in excess, settles rapidly. The analytical results are:

| | I. | II. | III. | Average. |
|---|---|---|---|---|
| Lead | 66.03 | 66.15 | 66.09 | 66.09 |
| $Fe(CN)_6$ | 34.07 | 33.98 | 33.85 | 33.97 |
| Potassium | 0.50 | 0.48 | 0.45 | 0.47 |
| | | | | 100.53 |

B. Solution neutral, ferrocyanide in excess, the precipitate settles slowly. It gave on analysis:

| | I. | II. | III. | Average. |
|---|---|---|---|---|
| Lead | 66.26 | 66.06 | 65.98 | 66.10 |
| $Fe(CN)_6$ | 33.54 | 33.77 | 33.90 | 33.70 |
| Potassium | 0.62 | 0.55 | 0.58 | 0.58 |
| | | | | 100.38 |

C. Solution slightly acid with acetic acid, lead in excess. The precipitate settles rapidly. On analysis the following results were obtained:

| | I. | II. | III. | Average. |
|---|---|---|---|---|
| Lead | 64.42 | 64.55 | 64.62 | 64.53 |
| $Fe(CN)_6$ | 35.48 | 35.33 | 35.37 | 35.39 |
| Potassium | 0.84 | 0.81 | 0.80 | 0.82 |
| | | | | 100.74 |

D. Solution slightly acid with acetic acid, ferrocyanide in excess. Precipitate settles rapidly. The results on analysis were almost identical with those obtained from the preceding precipitate.

| | I. | II. | III. | IV. | Average. |
|---|---|---|---|---|---|
| Lead | 64.43 | 64.28 | 64.38 | 64.58 | 64.42 |
| $Fe(CN)_6$ | 35.47 | 35.62 | 35.69 | 35.60 | 35.59 |
| Potassium | 0.82 | 0.76 | 0.86 | 0.79 | 0.81 |
| | | | | | 100.82 |

E. Solution strongly acid with acetic acid, ferrocyanide in excess. Precipitate settles badly. The results are:

| | I. | II. | Average. |
|---|---|---|---|
| Lead | 63.73 | 64.02 | 63.87 |
| $Fe(CN)_6$ | 35.51 | 35.02 | 35.26 |
| Potassium | 0.76 | 0.96 | 0.86 |

These and the following are results calculated from the determination of potassium, lead, and iron in undried portions and consequently, when calculated from the ratio of Fe : K : Pb, add up to 100 per cent.

F. Solution strongly acid with hydrochloric acid, ferrocyanide in excess, precipitated hot as usual.

| | I. | II. | Average. |
|---|---|---|---|
| Lead | 63.02 | 63.39 | 63.21 |
| $Fe(CN)_6$ | 34.74 | 34.48 | 34.61 |
| Potassium | 2.24 | 2.12 | 2.18 |

When the analysis is made on a sample dried to constant weight, it invariably adds up to a little over 100 per cent. This is probably caused by the fact that on drying, the precipitates become either bluish or greenish in color due to a slight decomposition so that the percentages of $Fe(CN)_6$ which are calculated from the iron are high.[1]

It is evident from these results that the precipitate varies in composition under different conditions of precipitation, and as the acidity increases the percentage of potassium increases and that of lead diminishes.

Also, that when the acidity is the same the composition is the same whether ferrocyanide or lead is in excess.

Berzelius[2] states that when formed in a neutral solution with potassium ferrocyanide in excess, the composition of the precipitate is $Pb_2Fe(CN)_6$. Using the most recent atomic weights this corresponds to a percentage composition of:

| | |
|---|---|
| Lead | 66.10 |
| $Fe(CN)_6$ | 33.90 |

Our results are, with lead in excess:

| | |
|---|---|
| Lead | 66.09 |
| $Fe(CN)_6$ | 33.97 |

[1] For the CN : Fe ratio is higher in $Fe(CN)_6$ than in $Fe_7(CN)_{18}$ or $Fe_5(CN)_{12}$.

[2] *Ann. Chem. Phys.*, **15**, 157 (1820).

With ferrocyanide in excess:

| | |
|---|---|
| Lead | 66.10 |
| $Fe(CN)_6$ | 33.70 |

The only statement we have found suggesting any variation in the composition of this ferrocyanide is by Gay-Lussac[1] that "the precipitate for however long a time it may have been washed, retains from 6–9 per cent. of ferrocyanide of potassium; of which it continues to give up a certain quantity to fresh portions of water." The conditions of this precipitation are not stated.

In order to compare these results with those obtained by titration, the following experiments were made. A solution of potassium ferrocyanide was very carefully standardized against metallic zinc and freshly ignited zinc oxide. The conditions being; bulk 200 cc., acidity 2 cc. concentrated hydrochloric acid, temperature about 80° C. Uranium acetate was used as an indicator on porcelain. An allowance of 0.3 cc. was made in each case for the excess necessary to affect the indicator. The results of six concordant determinations gave as the strength of this solution, 1 cc. = 0.005857 gram of zinc.

This solution was then used to titrate solutions containing known weights of lead as follows:

*Neutral Solution.*—Separate portions of metallic lead, of about 1 gram each, were dissolved in nitric acid, hydrochloric acid added and evaporated to complete dryness; the lead chloride was then dissolved in hot water diluted to 200 cc. and titrated. The titration in a neutral solution is not altogether satisfactory. Five determinations gave results varying from 0.02454 to 0.02461. Average, 0.02458.

*Acetic Acid Solution.*—Six determinations gave from 0.02450 to 0.02458; the average coinciding with the two most satisfactory titrations is 0.02454 gram.

*Hydrochloric Acid Solution.*—In a solution containing one drop of concentrated hydrochloric acid the results were from 0.02441 to 0.02446; average, 0.02444 gram. With 1 cc. of hydrochloric acid the results were unreliable on account of the solubility of the precipitate.

[1] Gmelin's "Handbook of Chemistry" (London, 1852), Vol. VII, p. 490.

Assuming that the precipitates formed are in one case $Zn_3K_2(Fe(CN)_6)_2$, and in the other $Pb_2Fe(CN)_6$ or that an amount of ferrocyanide which precipitates three atoms of zinc precipitates four of lead, the factor by which the zinc standard must be multiplied to give the lead standard is 4.218. This gives by calculation from the zinc standard, 0.0247 as the lead standard of the solution.

The amounts of lead precipitated per cubic centimeter in no case reach this value and although the variations are not so great as is shown from the analyses of the precipitates, they are in exactly the same order, and so confirm the statement that increase of acidity tends to diminish the percentage of lead in the precipitate.

Our results agree closely with Low's[1] statement: that a solution containing 10 grams per liter of crystallized potassium ferrocyanide will equal 10 milligrams of lead per cubic centimeter, and are at complete variance with a statement by Furman[2] that it requires 16 grams per liter for such a solution. Furman's figure is evidently based on the assumption that this value can be determined by a direct ratio between lead and zinc.

## CADMIUM FERROCYANIDE.

The potassium ferrocyanide solution, already described, was used to titrate a number of solutions containing cadmium under different conditions. Portions of cadmium oxide of 0.3 to 0.4 gram each were dissolved in hydrochloric acid, and evaporated to complete dryness, then dissolved in 200 cc. of hot water and titrated. It was found that uranium acetate on porcelain was very unsatisfactory as the precipitate reacts with the indicator as is the case with manganese, so that the end tests in these titrations were made on filter-paper placing the drops so that the precipitate of cadmium ferrocyanide did not come in contact with the uranium acetate.

The results in a neutral solution were not concordant, varying between 0.0071 and 0.00727 gram of cadmium per cubic centimeter.

In a solution containing 1 cc. of 50 per cent. acetic acid the

[1] This Journal, 15. 550 (1893).

[2] "Manual of Practical Assaying," p. 139.

results ran from 0.00699 to 0.00702 gram of cadmium; average, 0.0070 gram.

In a solution containing 1 to 2 cc. of concentrated hydrochloric acid the average of six determinations on cadmium oxide gave 1 cc = 0.007177 gram of cadmium; this was checked by four tests with metallic cadmium which gave 0.007165 gram, or a general average of 0.00717 gram. Another set was made with only a few drops of hydrochloric acid present; these gave almost the same results. With this solution it was found possible to use uranium acetate on porcelain but drops on filter-paper are a safer end-point for cadmium titrations.

As cadmium hydroxide is soluble in ammonia it was possible to extend the titration to an ammoniacal solution by using as an indicator a 4 per cent. solution of copper sulphate, as recommended by Moldenhauer[1] for zinc. The spots are made on filter-paper, as already described; the end-point, a red line, is distinct but not as delicate as with uranium acetate. An allowance of 0.9 cc. was made for the excess necessary to affect the indicator. Four tests gave the following values for 1 cc.: 0.00669, 0.00678, 0.00674, 0.00674; average, 0.00674 gram of cadmium per cubic centimeter.

The formula usually assigned to cadmium ferrocyanide is that given by Hermann:[2] $CdK_2Fe(CN)_6$; assuming that this is the composition of the precipitate, the ratio as regards ferrocyanide is $3Zn = 2Cd$, and the strength of the ferrocyanide solution used would be 1 cc. = 0.00671 gram cadmium. The results of the titrations do not agree with this value except those obtained in an ammoniacal solution.

Other formulas have been given for cadmium ferrocyanide. Dammer gives it the normal composition $Cd_2Fe(CN)_6$ and cites Wittstein[3] as his authority, but the original article gives neither formula nor analysis.

Wyrouboff[4] gives the composition under all conditions as $K_5Cd_5(Fe(CN)_6)_4$ which has been altered in Comey's "Dictionary," so as to satisfy the valence of the $Fe(CN)_6$ radical to $K_6Cd_5(Fe(CN)_6)_4$. Assuming that this is the precipitate formed, the

[1] *Chem. Ztg.*, **13**, 1220 (1889), and **15**, 223 (1891).
[2] *Ann. Chem. u. Pharm.*, **145**, 235 (1868).
[3] Büchner's *Repertorium der Pharm.*, **63**, 316-317.
[4] *Ann. chim. phys.* [5], 8, 449 (1878).

ratio as regards ferrocyanide becomes $6Zn = 5Cd$, and the strength of the solution used would be 1 cc. = 0.00838 gram cadmium.

Our results in acid solutions are intermediate between these values and indicate a variation in the composition of the precipitate between the formulas of Hermann and of Wyrouboff. They are confirmed by a statement by Mackay[1] that it requires about $2\frac{1}{2}$ per cent. less potassium ferrocyanide to precipitate cadmium than is required by the formula $CdK_2Fe(CN)_6$ or in other words the cadmium standard is higher than would be obtained by calculation. They are again in direct contradiction to the statement by Furman that the cadmium standard can be obtained from the zinc standard by direct proportion assuming that $2Zn = 2Cd$.

In order to ascertain the composition of cadmium ferrocyanide under different conditions analyses of the precipitates must, of course, be made. This work has already been started and while no results have yet been obtained the marked difference in the physical properties of the precipitates seems to confirm the variation in composition.

COLUMBIA UNIVERSITY,
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[CONTRIBUTION FROM THE LABORATORY OF THE NORTH CAROLINA AGRICULTURAL EXPERIMENT STATION.]

## THE DIGESTIBILITY OF SOME NON-NITROGENOUS CONSTITUENTS OF CERTAIN FEEDING-STUFFS.[2]

BY G. S. FRAPS.

Received June 16, 1900.

THE ether extract, protein, nitrogen-free extract, and crude fiber, which are determined in ordinary feeding-stuff analyses, are groups of compounds, and are composed of various substances with different properties and different coefficients of digestibility. The ether extract may contain (besides the true fats) waxes, cholesterin, phytosterin, lecithin, hydrocarbons, coloring-matters, etc. "Protein" includes amido compounds, acid amides, organic bases, ammonia, and nitrates, besides proteids of varied nature, one of which, nuclein, is entirely indiges-

[1] This Journal, 21, 940 (1899).

[2] This work was suggested to the author by Prof. W. A. Withers, Chemist of the Station. See Bulletin 172.

tible. The nitrogen-free extract may contain sugars, dextrin, gums, starches, pentosans, coloring-matters, organic acids, lignocellulose and cellulose, the two latter remaining in part in the crude fiber. The crude fiber contains cellulose, lignocellulose, etc. Considering the number of substances which may enter into the composition of the fodder-groups, and the variations which take place in the quantity present, it is not surprising that the digestibility of these groups differs greatly with different feeding-stuffs.

The digestibility of some of the proximate constituents of feeding-stuffs has been determined, or, more correctly, groups of proximate constituents, namely, the sugar group, the starch group, and the pentosan group. All three of these groups have not been determined on the same material. The work about to be described in this paper has given a basis for calculating the digestibility of certain proximate groups, which can be arranged in the following tentative order, according to their digestibility: Sugars, starches, pentosans, crude fiber, residual nitrogen-free extract, and pentosans in the crude fiber. The number of digestion experiments made is not large, but it is not believed that future experiments will materially modify the order above given. This Station expects to continue the work along this line.

The materials used in this work are from digestion experiments on sheep, one described in Bulletin 148 of this Station, six described in Bulletin 160, one not yet published. Excepting timothy hay No. 1, all figures are means of experiments with two sheep.

## DIGESTIBILITY OF SUGARS.

W. H. Jordan, J. M. Bartlett, and L. H. Merrill, at the Maine Experiment Station,[1] found that the sucrose and reducing sugars in alsike clover, white clover, blue joint, orchard grass, red top, timothy, wild oat grass, witch grass, buttercup, and white weed were completely digested. E. F. Ladd, at the New York (Geneva) Experiment Station,[2] found the sucrose and reducing sugars to be completely digested in alfafa hay, mixed hay, wheat bran, corn-meal, cottonseed-meal, linseed-meal, and oats; the

[1] Report 1888, 98.
[2] Report 1889, 149.

sucrose in turnips fed with mixed hay was digested only 78.7 per cent., the reducing sugars being completely digested. B. W. Kilgore and F. E. Emery, at the North Carolina Station,[1] found the reducing sugars completely digested in corn-fodder, crimson clover hay, cowpea vine hay, soja-bean silage, cottonseed, and cottonseed hulls. H. C. Sherman[2] found the glucose and sucrose (soluble carbohydrates) of wheat bran digested 96.7 per cent., the feces containing 0.7 per cent.

Twenty-three excrements from a number of digestion experiments made at this Station were tested for sugars in the usual way, after treating the solution with lead acetate. In twelve of them, traces of copper were reduced, corresponding to from 0.04 to 0.20 per cent. of sugars, with a mean of 0.09 per cent. This reduction is not believed to be caused by sugars, but by other reducing matters, as is plain from the following experiment: Excrement 1376, from corn silage, giving 0.15 per cent. apparent sugars; excrement 1377, from corn silage, 0.05 per cent. sugars; excrement 1411, from timothy hay, 0.20 per cent. sugars; and excrement 1437, from sorghum fodder, 0.14 per cent. sugars were taken. Fifty grams of each were digested with 500 cc. cold water, filtered, and washed with about 1000 cc. water. Basic lead acetate was added in excess, filtered, and the filtrate evaporated to about 25 cc. on a water-bath, organic matter separating. The lead was removed with sodium carbonate, filtered off, and the filtrate made up to 100 cc. Twenty-five cc., corresponding to 12.5 grams excrement, and about seventeen times as much as was used in the preliminary test, gave no trace of either sucrose or dextrose in any of the four excrements. The reducing substances probably separated during the evaporation. The traces of copper oxide were probably not due to reduction by sugars.

The twenty-three excrements were as follows: From crabgrass hay, crabgrass hay and pea-meal (2), crabgrass hay and corn bran (2), green rape (3), crabgrass hay and rice bran (2), cattail millet (2), sorghum fodder (2), crimson-clover hay, soja-bean silage, corn silage (4), timothy hay (2), corn fodder. In

[1] Technical Bulletin No. 4.
[2] This Journal, 19, 291.

the twelve materials and twenty-three experiments, sucrose and reducing sugars were completely digested.

Taking all the experiments into consideration, it is found that in thirty materials and forty-one experiments, reducing sugars are invariably digested completely, and in twenty-eight of the thirty materials, and thirty-nine of the forty-one experiments, sucrose is completely digested. The assertion that sugars are, as a rule, completely digested may be taken as established.

The determination of sugars is important with hays, and cotton-seed-meal; less so in the case of the starchy foods. Hays contain a moderate amount of sugars; for example,[1] red clover (average of 21) contains 6.36 per cent., timothy hay (average of 21) 8.44 per cent., sorghum 21 per cent., corn fodder 3.9 per cent.; cottonseed-meal contains 9.22 and 7.94 per cent. raffinose, being 33.5 and 32.9 per cent. of the nitrogen-free extract, respectively. If the sugar in the hays is subtracted from the nitrogen-free extract, and then the digestibility of the latter is calculated, a considerable decrease is often found. The digestibility of nitrogen-free extract, containing sugars, is 71.8 in alfafa hay; if sugar is subtracted, it is 68.5, a decrease of 4.6 per cent. With mixed hay, the decrease is from 55.5 to 40.4, a decrease of 27 per cent.; with timothy hay, from 60.3 to 53.5, or 11 per cent., and 56.2 to 51.1, or 9.1 per cent.; with green rape, from 93.8 to 92.5, or 1.4 per cent.; and with cottonseed-meal, from 61.5 to 42.5, the enormous decrease of 31 per cent. These figures may serve to emphasize the importance of determining sugars. The calculations and details of all these experiments are published in Bulletin No. 172 of this Station.

## DIGESTIBILITY OF PENTOSANS.

The furfural produced by distillation of feeding-stuffs with hydrochloric acid comes, for the most part, from pentosans; *i. e.*, bodies which yield pentose sugars on hydrolysis. Other bodies than true pentosans are found in plants, which are decomposed with formation of furfural, such as the oxycelluloses and lignocelluloses. The latter are usually described as mixtures of cellulose and incrusting substance, or lignin.

The true pentosans are, presumably, dissolved by dilute acids

[1] E. F. Ladd: *Am. Chem. J.*, 10, 49.

and alkalies, and hence are contained in the nitrogen-free extract, but the oxycelluloses and lignocelluloses are partly attacked by these reagents also. The furfural from the crude fiber may be considered as originating from the latter bodies, to which the name pseudopentosans may be given.

W. E. Stone[1] determined the digestibility of total pentosans in a number of feeding-stuffs, titrating the furfural distillate with phenylhydrazine, and using Fehling's solution as an indicator. The per cent. of pentosans digested was found to be: in timothy hay, 48.0 and 49.5 per cent.; ditto early bloom, 60.4 and 54.6 per cent.; ditto late cut, 62.8 and 48.2 per cent.; *Danthonia spicata*, 68.6 per cent.; *Agrostis vulgaris*, 70 per cent.; *Calamagrostis canadensis* 90.4 per cent.; *Triticum repens*, 59.9 per cent.; Hungarian grass, 68.2 per cent.; *Trifolium hybridum*, 56.8 per cent.; corn fodder, northern, 76.6 per cent.; ditto southern corn, 69.6 per cent.; timothy hay and sugar-beets, 71.3 per cent.; timothy hay and rutabagas, 57.1 per cent.; timothy hay and wheat bran, 45.6 per cent.; timothy hay and gluten meal, 59.1 per cent.; *Agrostis vulgaris* and wheat bran, 54.1 per cent.; ditto and wheat middlings, 64.9 per cent. Excluding *Calamagrostis canadensis*, the average digestibility of the pentosans in the nineteen substances is 60.3 per cent., with a minimum of 45.6 and a maximum of 71.3 per cent.

J. B. Lindsay and E. B. Holland[2] have determined the digestibility of pentosans in the following materials: Hay of mixed grasses, (a) 63 per cent., (b) 62 per cent.; Buffalo gluten feed, 78 per cent.; new process linseed-meal, 89 per cent.; old process linseed-meal, 84 per cent.; corn cobs, 62 per cent.; dried brewer's grains, 55 per cent; spring-wheat bran, 62 per cent.; winter-wheat bran, 64 per cent. The mean is 68.8 per cent.

H. C. Sherman[3] found the digestibility of pentosans in wheat bran to be 66.2 per cent.

Determination of the total pentosans and pentosans in the crude fiber (pseudopentosans) have been made in feeding-stuffs, wastes, and excrements from digestion experiments made at this Station. The method of determining pentosans used is, in

1 *Agr. Science*, 7, 6.
2 *Ibid.*, 8, 172.
3 This Journal, 19, 308.

brief, as follows: Three grams of substance in a side-necked flask on a wire gauze are distilled with 100 cc. of hydrochloric acid of 1.06 specific gravity. When 30 cc. have distilled over, 30 cc. of the acid are run into the flask through a separatory funnel in such a manner as to wash down the particles on its sides. The distillation is continued in this manner until the volume of the distillate is 360 cc. A sufficient quantity of phloroglucinol to precipitate all the furfural, is added, the volume made up to 500 cc., the precipitate collected on a Gooch filter, washed with 100 cc. water, dried to constant weight at 100°, and weighed. The time required to dry the precipitate is from seven to nine hours. Commercial phloroglucinol is used, and is purified by dissolving it in hydrochloric acid of 1.06 specific gravity and allowing the diresorcinol to crystallize out.

In the case of crude fiber, three grams of material were treated, in the usual way for the determination of crude fiber using, however, 300 cc. of the acid and 300 cc. of the alkali. The fiber was then distilled with acid, as described above.

The composition of the feeding-stuffs is given in the table.

COMPOSITION OF FEEDING-STUFFS.

(Dry Matter.)

| | Sugars. | Total pentosans. | Pentosans. | Pseudo-pentosans. | Residual N-free extract. |
|---|---|---|---|---|---|
| Timothy hay No. 1..... | 8.33 | 24.86 | 19.71 | 5.15 | 16.88 |
| Crabgrass hay No. 1..... | 1.89 | 26.25 | 21.90 | 4.35 | 21.40 |
| Crabgrass hay No. 2..... | 2.20 | 24.71 | 19.85 | 4.85 | 24.09 |
| Cowpea-meal..... | 5.66 | 6.83 | 6.83 | 0 | 52.20 |
| Corn bran..... | 2.93 | 25.15 | 25.15 | 0 | 41.36 |
| Green rape No. 1..... | 8.41 | 10.57 | 9.57 | 1.00 | 29.81 |
| Green rape No. 2..... | 7.03 | 8.71 | 8.04 | 0.67 | 26.04 |
| Rice bran..... | 1.56 | 10.88 | 9.88 | 1.00 | 40.31 |
| Cottonseed-meal..... | 7.94 | 7.83 | .... | .... | .... |

The pentosans in the crude fiber is, in timothy hay No. 1, 20.7 per cent. of the total pentosans; in timothy hay No. 2, 20.5 per cent.; in crabgrass hay No. 1, 18.4 per cent.; in crabgrass hay No. 2, 19.6 per cent.; in cowpea-meal and corn bran, none; in green rape No. 1, 9.5 per cent.; in green rape No. 2, 7.7 per cent., and in rice bran, 9.2 per cent. It is apparent that the crude fiber of hays contains a large percentage of the pentosans. The pentosans are distributed between the crude fiber and the nitrogen-free extract. The pentosans in the crude fiber

are not here regarded as true pentosans, but are called pseudopentosans; they are different from the pentosans in the nitrogen-free extract, although the line of separation between the two is an arbitrary one. The distribution and digestibility of the pentosans are given in the table. It is seen that from 0 to 21 per cent. of the pentosans are pseudopentosans, and that in four of the five cases the pseudopentosans are less digestible than the pentosans in the nitrogen-free extract. The digestibility of the total pentosans varies from 53 to 95 per cent.

DISTRIBUTION AND DIGESTIBILITY OF PENTOSANS.

| | Of 100 parts pentosans | | Digestibility of pentosans. | | |
|---|---|---|---|---|---|
| | True | Pseudo- | Total | True | Pseudo- |
| Timothy hay No. 1 | 79.3 | 20.7 | 55.8 | 58.1 | 46.9 |
| Timothy hay No. 2 | 79.5 | 20.5 | 55.9 | 57.0 | 52.0 |
| Crabgrass hay No. 1 | 81.6 | 18.4 | 63.1 | 61.0 | 69.9 |
| Crabgrass hay No. 2 | 80.4 | 19.6 | .... | .... | .... |
| Cowpea-meal[1] | 100.0 | 0 | 76.1 | 76.1 | .... |
| Corn bran[1] | 100.0 | 0 | 71.6 | 71.6 | .... |
| Green rape No. 1 | 90.5 | 9.5 | 94.6 | 95.7 | 84.6 |
| Green rape No. 2 | 92.3 | 7.7 | 91.9 | 93.2 | 75.9 |
| Rice bran[1] | 90.8 | 9.2 | 53.5 | 57.3 | .... |

DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

The composition and digestibility of the nitrogen-free extract is given in the table below. The residual nitrogen-free extract is the total nitrogen-free extract less sugars and pentosans. It varies in quantity from 47 to 85 per cent. of the nitrogen-free extract.

COMPOSITION AND DIGESTIBILITY OF NITROGEN-FREE EXTRACT.

| | In 100 parts | | | Digestibility. Sugars 100 per cent. | |
|---|---|---|---|---|---|
| | Sugars. | Pentosans. | Residue. | Pentosans. | Residue. |
| Timothy hay No. 1 | 14.9 | 35.2 | 49.9 | 58.1 | 50.1 |
| Timothy hay No. 2 | 10.5 | 41.6 | 47.9 | 57.0 | 46.0 |
| Crabgrass hay No. 1 | 4.2 | 48.4 | 47.4 | 61.0 | 32.7 |
| Crabgrass hay No. 2 | 4.8 | 43.0 | 52.2 | .... | .... |
| Cowpea-meal[2] | 4.8 | 10.6 | 84.6 | 76.1 | 97.4 |
| Corn bran[2] | 4.2 | 36.2 | 59.6 | 71.6 | 86.1 |
| Green rape No. 1 | 15.2 | 20.6 | 64.2 | 95.7 | 91.4 |
| Green rape No. 2 | 19.8 | 18.9 | 61.3 | 93.2 | 86.5 |
| Rice bran[2] | 3.0 | 19.1 | 77.9 | 57.3 | 85.0 |

[1] Calculated from ration with crabgrass hay.

[2] Digestibility calculated from ration with crabgrass hay.

In the timothy hays, the crabgrass hay, and the green rape, the order of digestibility is: sugars, pentosans, residue. In the cowpea-meal, the corn bran, and the rice bran, the order is: sugars, residue, pentosans, but this residue consists most largely, if not entirely of starch, so that we may say that starch is more digestible than pentosans. The order of digestibility of the components of the nitrogen-free extract is, then,—sugars, starch, pentosans, and residue.

### DIGESTIBILITY OF CRUDE FIBER.

Crude fiber contains from 0 to 21 per cent. of the total pentosans, sometimes as much as 42 per cent.[1] The table below exhibits the composition and digestibility of the crude fiber. In four of the five cases, the pseudopentosans are less digested than the residue, and the residue more so than the total crude fiber, although the difference is not great. The digestibility of the residual nitrogen-free extract has been placed in the table for purposes of comparison. With timothy hay, and crabgrass hay, it is less digestible than the residual crude fiber, in one case more, the other two less, digestible than the pseudopentosans. With the green rape, its digestibility is slightly greater than that of the residual crude fiber. With the starchy foods, its digestibility is greater, as a matter of course, since it consists for the most part of starch.

COMPOSITION AND DIGESTIBILITY OF CRUDE FIBER.

| | In 100 parts | | Digestibility. | | | Residual nitrogen-free extract. |
|---|---|---|---|---|---|---|
| | Pseudo-pentosans. | Residue. | Total. | Pseudo-pentosans. | Residue. | |
| Timothy hay No. 1 | 9.2 | 90.8 | 52.3 | 46.9 | 53.3 | 50.1 |
| Timothy hay No. 2 | 14.4 | 85.6 | 53.8 | 52.0 | 54.1 | 46.0 |
| Crabgrass hay No. 1 | 13.0 | 87.0 | 67.3 | 69.9 | 67.0 | 32.7 |
| Crabgrass hay No. 2 | 13.4 | 86.6 | .... | 62.5[2] | .... | .... |
| Cowpea-meal[3] | 0 | 100.0 | 39.2 | .... | 39.2 | 97.4 |
| Corn bran[1] | 0 | 100.0 | 50.8 | .... | 50.8 | 86.1 |
| Green rape No. 1 | 7.7 | 92.3 | 90.0 | 84.6 | 90.4 | 91.4 |
| Green rape No. 2 | 6.3 | 93.7 | 84.0 | 75.9 | 84.6 | 86.5 |
| Rice bran[1] | 8.3 | 91.6 | 19.1 | .... | 19.1 | 85.0 |

While, therefore, the order in the series, sugar, starch, pentosans, and residual nitrogen-free extract, is subject to little doubt,

[1] J König: *Landw. Versuch. Stats.*, **48**, 93.
[2] Calculated from ration with crabgrass hay.
[3] Calculated from ration with cowpea-meal.

and the order, residual crude fiber, pseudopentosans, is not doubtful, the combination of the two series is more doubtful. The approximate arrangement in the order of digestibility would be sugar, starch, pentosans, residual crude fiber, residual nitrogen-free extract, pseudopentosans, the position of residual crude fiber and pseudopentosans being subject to change.

It is seen that the residual nitrogen-free extract, in three hays at least, is less digestible than the residual crude fiber. Is this an actual or an apparent difference? It is assumed in digestion experiments that those fodder groups which are not digested pass through unchanged, an assumption that must be modified for the nitrogenous matters and the ether extract, since products of metabolism appear in the excrement which fall into these two groups. It is quite possible that crude fiber undergoes some change that renders it soluble in acids or alkalies.

Crude fiber may disappear:

(1) By formation of soluble compounds and resorbtion;

(2) By decomposition to carbon dioxide and marsh gas;

(3) By decomposition with the formation of carbon dioxide and marsh gas, and soluble products which are resorbed;

(4) By decomposition with formation of products which are not resorbed, and are soluble in hot acids or alkalies, hence goes into the nitrogen-free extract.

Besides the sugars, starches, gums, etc., the nitrogen-free extract of hays is composed of the less resistant portions of the cell walls, partly made up of pentosans. Our digestion experiments seem to show that the older and more resistant cellular structures (crude fiber) are in many cases digested to a greater extent than the younger and less resistant. To avoid this difficulty, it has been assumed that the more resistant portions are converted by bacteria into gases and soluble products, which are resorbed. This may be part of the truth, but not all of it. We would naturally suppose the less resistant portions—in the nitrogen-free extract—to be attacked by the bacteria first, and the nitrogen-free extract ought to be digested more completely than the crude fiber. The explanation that seems probable is, that the crude fiber and undigested nitrogen-free extract, remaining several days in the intestines under very favorable conditions for the action of micro-organisms, are decomposed, with formation

of gases, of soluble products which are resorbed, and of insoluble products which pass into the excrement, and, being soluble in acids or alkalies, appear in the analysis as nitrogen-free extract. The digestibility of the nitrogen-free extract would appear less than it really is, and that of the crude fiber, greater.

## ANALYSIS OF FEEDING-STUFFS.

This work has shown that if we take the sugars, starch, and pentosans from the nitrogen-free extract, the residue is sometimes more, sometimes less digestible than the crude fiber, and often the difference is not great. For this reason, in the analysis of feeding-stuffs, it is of more importance to determine sugar, starch, and pentosan, than to determine crude fiber.

E. Schulze[1] has proposed that, in addition to the determination of crude fiber, the non-nitrogenous matters insoluble in ether, alcohol, water, and diastase solution be determined. The residue would consist of the material of cell walls, insoluble proteids, and a portion of the ash. It is corrected for the ash and proteids. This method should not be used in digestion work, since insoluble nitrogen-free extract or crude fiber may have become soluble during its several days' stay in the animal. It may be used when a knowledge of the properties of a feeding-stuff is desired quickly.

## SUMMARY.

1. Sugars are found in all feeding-stuffs, are completely digested, as a rule, and their determination is of especial importance in the case of hays and cottonseed-meal.

2. The average digestibility of pentosans in thirty-four samples is 64.2. The average for timothy hay (eight samples) is 53.9.

3. The constituents of the nitrogen-free extract may be arranged in the following order according to their digestibility: (1) sugars, (2) starch, (3) pentosans, (4) residue.

4. The pseudopentosans of crude fiber are less digestible than the residue. The residue is sometimes more, sometimes less digested than the residual nitrogen-free extract.

5. Crude fiber may be changed during digestion so as to appear as nitrogen-free extract in the excrement.

6. The determination of sugar, starch, and pentosans is more important than that of crude fiber.

May, 1900.

1 *Landw. Versuch-Stats.*, **49**, 434.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE, NO. 34.]

# ON THE HYDROCARBONS IN HEAVY TEXAS PETROLEUM.[1]

BY CHARLES F. MABERY AND D. M. BUCK.

Received June 15, 1900.

THE heavy petroleums that hitherto have been looked on as only fit for fuel are capable, if properly refined, of yielding valuable products. This is especially true of the deposits recently exploited in Wyoming, Texas, and in other sections. The Corsicana oil in Texas has been shown by Mr. Clifford Richardson to yield an oil that may be refined into gasoline, burning oil, and other products ordinarily obtained from light petroleums. Large areas of oil territory have recently been developed in Texas that yield oils of higher specific gravity, and that are of value for what they contain of the higher products. The rapid development of Texas oil territory bids fair to advance the state into an equivalent place with California as oil-producing territory.

As to the hydrocarbons which compose the heavy Texas oil, nothing whatever has hitherto been known. It is practically impossible to separate any of its constituents by the ordinary method of distillation. This examination of the Texas oil was undertaken with the purpose of ascertaining the principal series of hydrocarbons which compose the crude oil.

The specimen was obtained from a large territory owned by the Forward Reduction Company, of this city. The crude oil was very thick and dark in color. Its specific gravity at 20° was 0.9500. A determination of sulphur by the Carius method gave 0.94 per cent. These heavy oils almost invariably contain water suspended, and it is almost impossible to remove the water by drying, and the oil can not be distilled while it contains water on account of violent bumping. Under atmospheric pressure, scarcely any of the oil distilled below 240°. After drying by standing a long time in a warm place with fused calcium chloride, when distilled in vacuo under 13 mm. pressure, the distillates collected in the following proportions and gave the specific gravity annexed:

[1] The work in this paper was the subject of a thesis by Mr. Buck for the degree of Bachelor of Science.

| 150° | 150°–230° | 230°–300° | Above 300° |
|---|---|---|---|
| 10 per cent. | 32 per cent. | 21 per cent. | 37 per cent. |
| 0.8753 | 0.9222 | 0.9602 | Very thick. |

Next 500 grams were distilled under 25 mm. up to 310°, leaving a residue in the flask of 175 grams. The distillations were repeated several times until larger quantities collected at the following temperatures:

| 125°–130° | 140°–145° | 160°–165° | 175°–180° | 195°–200° | 215°–220° |
|---|---|---|---|---|---|
| 0.8744 | 0.8848 | 0.8986 | 0.9095 | 0.9231 | 0.9373 |

| 225°–230° | 240°–245° | 270°–275° |
|---|---|---|
| 0.9432 | 0.9478 | 0.9559. |

For the removal of benzene hydrocarbons and other impurities, the constituents with lower boiling-points were treated several times with fuming sulphuric acid, then washed with sodium hydroxide and water. The remaining oil was nearly colorless. In order to prevent decomposition of the less stable constituents with higher boiling-points by the fuming acid, the heavy oil was dissolved in light gasoline. After the solution became colorless, the gasoline was distilled off, leaving the heavy oil. By this method, it is possible to purify any of the distillates with high boiling-points without decomposition.

The fraction 125°–130° (25 mm.), after treatment with the fuming acid, gave as its specific gravity 0.8711, very little less than the specific gravity of the unpurified distillate, indicating that very little else was contained in this fraction but the principal hydrocarbon. A determination of the molecular weight of the oil at the freezing-point of benzene gave 196; required for $C_{14}H_{26}$, 194. The index of refraction was also determined and the molecular refraction calculated from it was 62.39; required for $C_{14}H_{26}$, 62.34. A combustion of the oil gave 86.56 per cent. of carbon, and 13.46 per cent. of hydrogen; required for $C_{14}H_{26}$, carbon 86.59, hydrogen 13.41.

The fraction 140°–145° (25 mm.) was purified in the same manner, and the same determinations were made. The results of the determinations of carbon and hydrogen, molecular weight determinations and molecular refraction led to the formula of the hydrocarbon $C_{15}H_{28}$.

By the same method of purification, the fraction 160°–165° (25 mm.) was obtained nearly colorless, and it then gave as its specific gravity 0.8894, only slightly less than the specific gravity of the unpurified oil. Determinations of carbon and hydrogen, of its molecular weight and molecular refraction, gave results leading to the formula $C_{16}H_{30}$.

After treatment with the fuming acid, the fraction 175°–180° (25 mm.) gave as its specific gravity 0.8966, essentially the same as that of the unpurified oil. The formula established by the same determinations as the others was $C_{17}H_{32}$.

The specific gravity of the fraction 195°–200° (25 mm.), after purification with fuming sulphuric acid, was 0.9070. Determinations of carbon and hydrogen, and molecular weight, led to the formula $C_{19}H_{36}$, although the low percentage of hydrogen indicated that the distillate contained some of the hydrocarbon with less hydrogen. The distillate 215°–220° (25 mm.) gave as its specific gravity, after purification, 0.9163. Its formula, established by analysis and determination of molecular weights, is $C_{21}H_{38}$.

The fraction 240°–245° (25 mm.) gave as its specific gravity 0.9306. No other determinations were made of this oil than its molecular weight, which corresponded to the formula $C_{23}H_{42}$. The fraction 270°–275° (25 mm.) was extremely viscous, and could be purified only by dissolving in gasoline. It gave a clear, slightly yellow oil, with a specific gravity 0.9410, practically the same as the unpurified distillate. Determinations of carbon and hydrogen, of molecular weight and molecular refraction, corresponded to the formula $C_{25}H_{46}$.

It appears, therefore, that this heavy Texas oil contains hydrocarbons from $C_{14}H_{26}$ to $C_{19}H_{36}$ of the series $C_nH_{2n-2}$, and higher hydrocarbons $C_{21}H_{38}$ to $C_{25}H_{46}$ of the series $C_nH_{2n-4}$. From the slight changes in specific gravity after thorough agitation with fuming sulphuric acid, it appears that these condensed methylenes constitute the chief body of the crude oil which distils within these limits. The first series is satisfied by assuming that the molecule is composed of two methylene rings connected in the same manner as diphenyl, with a sufficient number of methyl side-chains to account for the formula or with connecting carbon atoms between the rings. The study of the constituents

of Texas, California, and Canadian petroleums, with high boiling-points, is now in progress.

A summary of the results obtained in the examination of this petroleum is given in the following table:

| | B. P. (25 mm.) | Sp. gr. | Index of refraction. | Molecular refraction | |
|---|---|---|---|---|---|
| | | | | Calculated. | Found. |
| $C_{14}H_{26}$ | 125°–130° | 0.8711 | 1.4713 | 62.34 | 62.39 |
| $C_{15}H_{28}$ | 140°–145° | 0.8788 | 1.4746 | 66.94 | 66.70 |
| $C_{16}H_{30}$ | 160°–165° | 0.8894 | 1.4672 | 71.55 | 69.40 |
| $C_{17}H_{34}$ | 175°–180° | 0.8966 | 1.4721 | 76.14 | 73.85 |
| $C_{19}H_{36}$ | 195°–200° | 0.9020 | 1.4928 | 85.35 | 84.70 |
| $C_{21}H_{38}$ | 215°–220° | 0.9163 | 1.4979 | 92.46 | 92.91 |
| $C_{25}H_{46}$ | 270°–275° | 0.9410 | 1.5152 | 110.87 | 111.00 |

[CONTRIBUTION FROM THE LABORATORY OF HYGIENE, UNIVERSITY OF PENNSYLVANIA.]

## AN EXPERIMENTAL STUDY OF THE GAS-PRODUCING POWER OF BACILLUS COLI COMMUNIS UNDER DIFFERENT CONDITIONS OF ENVIRONMENT.

BY MARY ENGLE PENNINGTON AND GEORGE C. KÜSEL.

Received June 29, 1900.

THE power which some bacteria possess of liberating certain gaseous elements and compounds from suitable culture media has been the subject of a number of investigations. These investigations have brought to light many interesting facts, and have established methods of diagnostic value based upon gas production. Dr. Theobald Smith, in the account of his now classic experiments upon fermentation, has given a number of species which produce gases, the necessary conditions, quantity of gas produced, etc. Various analyses are on record, also, of the gas liberated, these analyses being more or less detailed depending upon the point of view of the investigator and the time when the work was done. Among the earlier workers we find, generally, that they were content with the determination of the amount of carbon dioxide. The residual gas, being found to be explosive, was accepted as hydrogen.

Later studies have been made with more care, and in consequence the presence of other gases has been recognized. Pammel and Bennett[1] have studied the action of several gas-producing organisms with especial attention to their behavior toward

[1] This Journal, 18, 157 (1896).

different sugars; namely, glucose, cane-sugar, and lactose. They mention the fact that the first portions of escaping gas are nearly pure hydrogen, but are inclined to ascribe this to the absorptive power for carbon dioxide possessed by the medium. The culture period for each experiment is given, and the analytical data, obtained by growing the organisms in various media, are compared, but nothing further regarding the progressive alteration in the composition of the gas formed is noted.

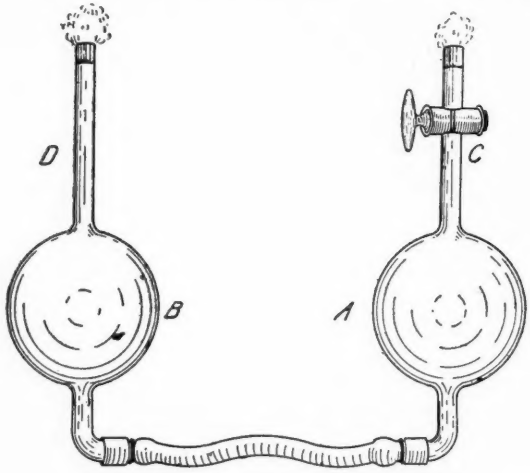
Some fermentation work with *Bacillus coli communis* which has been done in this laboratory, led us to believe that a change in the composition of the gas does occur with the advancing age of the culture and, also, that appreciable quantities of gases other than hydrogen and carbon dioxide are formed. The work in this laboratory also indicated that gas production by *Bacillus coli communis* in glucose bouillon in the usual saccharimeter tube is not so constant, either in relation to time of gas production or of the amount produced, as is generally believed. It seemed advisable, therefore, to cultivate this organism under the most concordant conditions possible, and to submit the gases produced to a careful chemical examination.

The chemist who undertakes quantitative chemico-bacteriological work has found in the past, and still finds, a source of error which at present seems insurmountable. This error lies in the quantity and quality of the inoculating material. Wherever inoculations are to be made the most careful work of trained eyes and skilled hands may yet leave a margin, plus or minus, of untold thousands of organisms, for with cells so prolific as are bacteria a small difference to-day is enormous to-morrow. Not only, too, must we consider the number of active organisms produced, but the waste products of those cells which are already dead may exert an appreciable influence upon later comers.

The gas-producing ability certainly varies considerably with the age of the culture. Many trials have demonstrated that *Bacillus coli communis* made upon nutrient agar are most active, so far as gas production is concerned, when three days old, the organisms having been kept at a temperature of 37° C. Older cultures, as a rule, produce less gas. This may be due to a decreased vitality of the germ from lack of food supply or from noxious waste products. In all of the experimental work given

below a three days' slant culture on agar was used as the seeding material.

After many trials with the various forms of apparatus for the collection and isolation of the gases generated by bacteria the following method was devised and used exclusively. The advantage of this form of apparatus is that it is easily handled, cleaned, and sterilized, besides being perfectly tight. That it is




exceedingly simple will be seen from the accompanying diagram. *A* is a glass bulb of 250 cc. capacity having an inlet, *C*, three inches long, into which a glass stop-cock is fused and an outlet *D*, of the same length, bent at right angles about one inch below the bulb. *B* is a like bulb except that the stop-cock is omitted. Heavy walled rubber tubing connects these two bulbs and is closely wired, both outlets being roughened to facilitate this. The inlets are plugged with cotton-wool, when the apparatus may be sterilized in an autoclave.

In the experiments to be described exactly 250 cc. of the desired culture medium were admitted through *D* the stop-cock of *C* being open. The level was then adjusted until the bore of the stop-cock was just filled. The cock was turned, and the apparatus, so far as *A* was concerned, was tight. Resterilization

in an autoclave at 45 pounds' pressure rendered the apparatus fit for inoculation. This was performed either by slipping a platinum wire through the stop-cock bore until it met the medium, or, as we preferred, by placing a definite number of drops of a suspension culture in the inlet tube *C* and drawing them into the bulb by lowering *B*.

As the organisms multiply, the gas collects in *A* displacing the liquid and forcing it over into *B*. The flexible connection between the two bulbs enables one to readily adjust the levels so that undue pressure, which checks fermentation, is obviated. The bulbs have been allowed to stand for days with bulb *B* depressed to its fullest extent but not the slightest inward leakage has been detected. When the experiments were being conducted a slight pressure in *A* was maintained as an additional precaution, so that the leak, if any, should be outward.

All the experiments were conducted at an incubator temperature, 37° C. The media were made with the greatest exactness possible. Commercial peptone, glucose, and salt were carefully dried and weighed accurately. When bouillon was desired Liebig's "*Extractum Carnis*" was used. The reaction of the medium was always neutral at the beginning of the experiment. Tenth-normal sodium hydroxide was used for this neutralization, phenolphthalein being the indicator. The gases were withdrawn from the bulb after cooling the latter to 18° to 19° C. and analyzed over mercury in a Hempel apparatus. Hydrogen was determined by explosion with oxygen. Hydrocarbons were determined by residual carbon dioxide. Nitrogen was found by difference. Heavy hydrocarbons were sought, but were not detected. All results are expressed in percentages. The amount of gas produced did not, as a rule, permit of more than one accurate carbon dioxide analysis. After absorbing the carbon dioxide, however, duplicate determinations of hydrogen, nitrogen, and methane were made. To exclude the personal error all the analyses were made by one person. When the variation in the results were large the experiments were submitted to a bacteriological investigation, but the cultures were found to be pure.

### NITROGEN AND METHANE.

A series of bulbs were filled as above described with neutral

bouillon containing 1 per cent. peptone, 0.5 per cent. sodium chloride, 0.5 per cent. Liebig's beef extract, and 1.5 per cent. glucose. The individual bulbs were analyzed at the expiration of the periods indicated in the table.

TABLE I.

*Series 1.*

| No. | Duration of experiments. Hours. | Carbon dioxide. Per cent. | Hydrogen. Per cent. | Methane. Per cent. | Nitrogen. Per cent. | Total volume. cc. |
|---|---|---|---|---|---|---|
| 1.... | 72 | 26.6 | 65.3 | 4.30 | 3.8 | 93 |
| 2.... | 72 | 26.45 | 65.82 | 3.61 | 4.12 | 64 |
| 3.... | 144 | 28.48 | 65.83 | 1.13 | 4.56 | 80 |
| 4.... | 168 | 23.75 | 70.13 | 1.15 | 4.97 | 67.8 |
| 5.... | 192 | 23.59 | 69.88 | 2.38 | 4.95 | 85 |
| | | | *Series 2.* | | | |
| 1.... | 36 | 34.30 | 63.20 | 1.00 | 1.30 | 82 |
| 2.... | 60 | 33.83 | 62.69 | 1.86 | 1.62 | 93.4 |
| 3.... | 84 | 27.03 | 69.88 | 1.02 | 2.07 | 83 |
| | | | *Series 3.* | | | |
| 1.... | 48 | 34.00 | 63.00 | 1.5 | 1.5 | 93 |
| 2.... | 72 | 27.5 | 66.3 | 3.00 | 3.2 | 98 |
| 3.... | 120 | 28.00 | 66.5 | 2.00 | 3.5 | 90 |

According to Table I, in addition to the carbon dioxide and hydrogen, the gases usually present, we find also nitrogen and methane. These gases were invariably found, and their presence in such appreciable quantities is of interest. Grimbert[1] has cultivated *Bacillus coli communis* in the presence of amido bodies, nitrates and nitrites, and states that amides are necessary if denitrification processes are to continue. In Grimbert's experiments sugar was not mentioned, the study being made in nitrated, or amidated, peptone solutions exclusively. In Bennett and Pammel's work we find no mention of nitrogen or methane in the gas produced. Wolff,[1] in a recent paper on denitrification, states that this organism reduces a nitrated peptone—glucose medium, giving nitrites.

Frequent repetition of our experiments, where no nitrates were added, with every possible precaution against admixture of air, gave invariably some nitrogen. The question therefore arose: Does the presence of air in bulb *B* affect the nitrogen production?

[1] *Ann. d. l'Inst.*, Pasteur, 13, 67 (1889).
[2] *Hygien. Rundsch.*, 9, 1169.

While fermentation is active the tendency would be to carry the organisms out of the field of activity (bulb *A*) and a backward migration cannot be very extensive. But at the close of the active period the organisms in *B*, may find their way into *A* again. Do they, from their contact with the oxygen at the surface of the liquid in *B*, become so modified physiologically that they alter the usual course of fermentation? To determine this point the following experiments were made in which all oxygen was excluded.

The apparatus above described was filled and sterilized in the usual manner. A Geissler potash bulb containing a freshly prepared pyrogallol and sodium hydroxide solution was attached to *B*, and a wash-bottle rigged flask, containing a like solution, was attached to *A*; the stop-cock was then opened, the level of *A* raised and the liquid allowed to flow into *B*, until the bulb was quite full. The air entering *A* was, of course, deprived of oxygen by the pyrogallate in the wash-bottle flask. The relative levels were next altered and bulb *A* refilled. The air in *B* was free from oxygen and remained so as indicated by testing over active phosphorus. The gas produced under such conditions still showed nitrogen, but we were surprised to find that hydrocarbons had disappeared (see Table II).

TABLE II.

*Series 1.*

| No. | Duration of experiment. Hours. | Carbon dioxide. Per cent. | Hydrogen. Per cent. | Methane. Per cent. | Nitrogen. Per cent. | Total volume. cc. |
|---|---|---|---|---|---|---|
| 1 | 40 | 30.00 | 67.80 | ..... | 2.20 | 82.0 |
| 2 | 64 | 28.91 | 67.53 | ..... | 3.56 | 83.0 |
| 3 | 86 | 28.00 | 66.99 | ..... | 5.01 | 83.2 |

*Series 2.*

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | 22 | 34.70 | 63.58 | ..... | 1.72 | 83 |
| 2 | 36 | 36.80 | 60.10 | ..... | 3.10 | 97 |
| 3 | 64 | 36.00 | 59.18 | ..... | 4.82 | 94 |

Series 1 and 2 of Table II were made with glucose bouillon of the composition given, and, except that the series were started on different days, were as exactly alike as possible. The results show well the marked variation which frequently appears, and which will be again met with in the course of this paper.

Control bulbs without the pyrogallate tubes were made in each case, and the analyses always showed hydrocarbons to be present. Hence we find that the entire exclusion of oxygen does not modify the nitrogen production in the least but that under such circumstances hydrocarbons are not produced.

In the foregoing experiments the organisms had a large supply of amido nitrogen on hand in the form of meat extractives. They had, also, the proteid nitrogen of the peptone. Commercial peptone varies considerably in composition and contains always more or less amido nitrogen. If the organisms are able to reduce the nitrogen of the extractives only we would expect to find much less nitrogen in a peptone-glucose solution than in one containing meat extractives in addition to the other constituents.

To determine to what extent these added meat extractives enter into the nitrogen evolved, the following series of bulbs were made with a culture medium composed of 1 per cent. peptone (Witte's) containing 1.5 per cent. glucose and 0.5 per cent. salt. The pyrogallate bulbs were not attached.

TABLE III.

| No. | Duration of experiment. Hours. | Carbon. dioxide. Per cent. | Hydrogen. Per cent. | Methane. Per cent. | Nitrogen. Per cent. | Total volume. cc. |
|---|---|---|---|---|---|---|
| | | | *Series 1.* | | | |
| 1 | 24 | 34.80 | 65.11 | .... | 0.09 | 100.0 |
| 2 | 48 | 30.2 | 62.83 | 1.63 | 5.34 | 97.4 |
| 3 | 120 | 28.11 | 64.6 | 1.80 | 5.49 | 86.0 |
| | | | *Series 2.* | | | |
| 1 | 46 | 35.58 | 60.34 | 1.34 | 2.74 | 97.8 |
| 2 | 84 | 32.00 | 61.39 | 1.00 | 4.54 | 94.8 |
| 3 | 140 | 30.00 | 62.72 | 1.78 | 5.50 | 98.0 |
| 4 | 144 | 30.41 | 62.88 | 1.77 | 4.94 | 96.0 |

Bulb No. 1 of Series 1, Table II, is the only experiment in which we have failed to detect nitrogen in appreciable amounts. It will be noticed that this bulb also lacks methane. The experiment was carried out in strict accord with the other members of the series, the medium being the same preparation, the inoculation from the same suspension culture. The reason for this variation is unexplained.

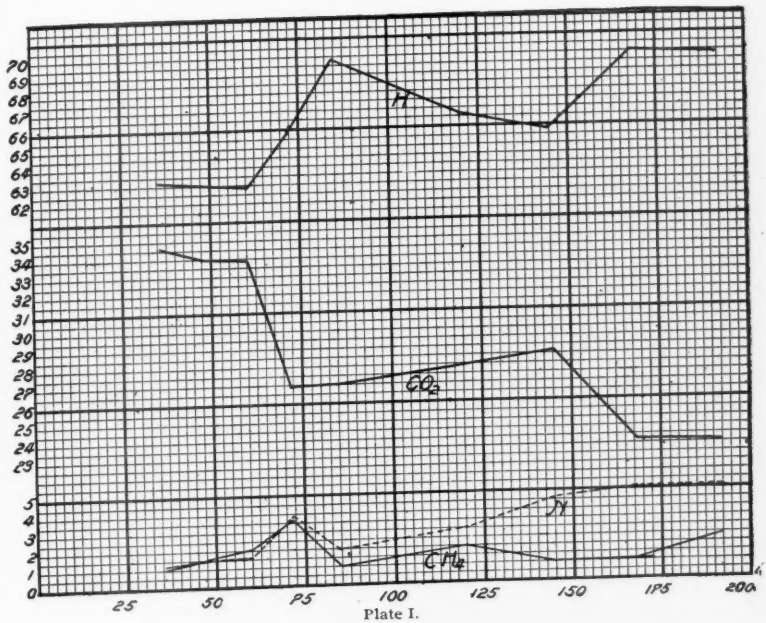



Plate I.

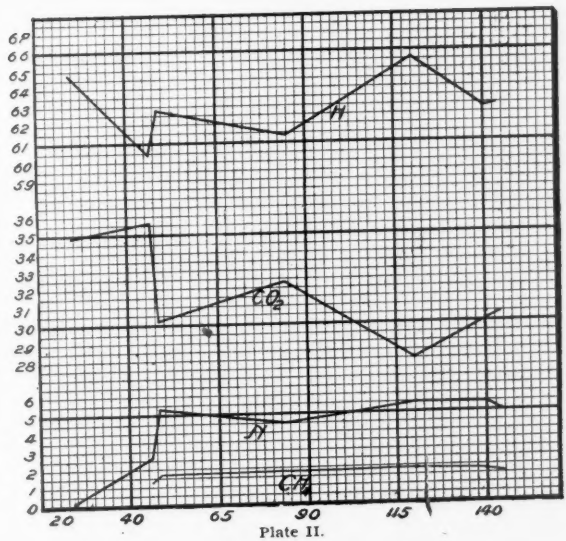



Plate II.

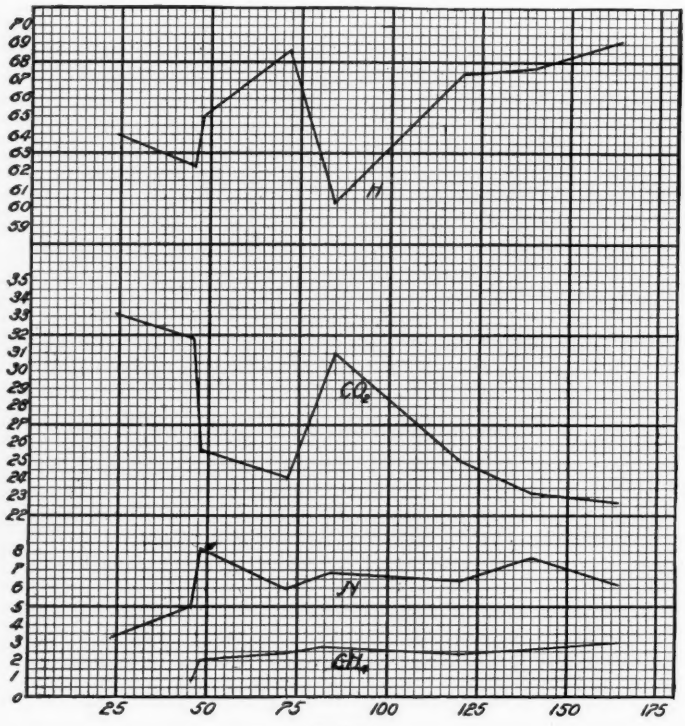



Plate III.

A comparison of the nitrogen obtained with and without the addition of extractives shows no appreciable nitrogen difference. If the amido nitrogen only is liberated we have in bulb 4 of Series 2 a quantity of nitrogen corresponding to 0.0184 gram of creatine. According to Allen,[1] Liebig's *Extractum Carnis* contains 29.32 per cent. meat bases. As 5 grams of the extract were added to 1 liter of the medium we have about 1.46 gram of extractives; or, as each bulb was supplied with 250 cc. of the fluid, 0.366 gram was available in each experiment. A very small quantity of amido nitrogen then is split off.

Because of the variability of peptones of different makes another sample, one obtained from Merck, was subjected to experiment.

[1] "Commercial Organic Analysis," Vol. IV, p. 311.

After careful drying it was made into a 1 per cent. solution containing salt and glucose as before. As in the similar experiments with Witte's peptone, extractives were omitted.

TABLE IV.

*Series 1.*

| No. | Duration of experiment. Hours. | Carbon dioxide. Per cent. | Hydrogen. Per cent. | Methane. Per cent. | Nitrogen. Per cent. | Total volume. cc. |
|---|---|---|---|---|---|---|
| 1..... | 24 | 33.41 | 64.07 | ... | 2.52 | 52.0 |
| 2..... | 48 | 25.77 | 64.98 | 2.00 | 7.25 | 50.0 |
| 3..... | 72 | 24.16 | 68.60 | 2.18 | 5.06 | 57.0 |
| 4..... | 120 | 24.89 | 67.36 | 2.35 | 5.40 | 53.0 |
| | | | *Series 2.* | | | |
| 1..... | 46 | 31.80 | 62.33 | 1.93 | 3.94 | 47.6 |
| 2..... | 84 | 31.06 | 60.33 | 2.77 | 5.84 | 93.6 |
| 3..... | 140 | 23.15 | 67.69 | 2.60 | 6.56 | 50.0 |
| 4..... | 164 | 22.69 | 69.10 | 3.10 | 5.11 | 57.6 |

With this sample of peptone there was a marked fall in the amount of gas produced, only about one-half the usual quantity being obtained. Bulb 1, of Series 1, Table IV, had made no methane at the end of twenty-four hours, but at the expiration of forty-eight hours, 2 per cent. was present in No. 2. The amount of carbon dioxide is distinctly less than that usually found.

VARIATION IN AMOUNT OF GASES PRODUCED.

A study of the results which have been obtained discloses an interesting relation from the standpoint of time variation. Table I, Series 1, 2, and 3, were made under conditions as concordant as possible and should therefore be comparable. Uniting these three tables into one we get the following :

TABLE V.

| No. | Duration of experiment. Hours. | Carbon dioxide. Per cent. | Hydrogen. Per cent. | Methane. Per cent. | Nitrogen. Per cent. | Total volume. cc. |
|---|---|---|---|---|---|---|
| 1..... | 36 | 34.50 | 63.20 | 1.00 | 1.30 | 82.0 |
| 2..... | 48 | 34.00 | 63.00 | 1.5 | 1.50 | 93.0 |
| 3..... | 60 | 33.83 | 62.69 | 1.86 | 1.62 | 93.4 |
| 4..... | 72 | 26.6 | 65.3 | 4.30 | 3.80 | 98.0 |
| 5..... | 72 | 27.5 | 66.3 | 3.00 | 3.20 | 98.0 |
| 6..... | 72 | 26.45 | 65.82 | 3.61 | 4.12 | 64.0 |
| 7..... | 84 | 27.03 | 69.88 | 1.02 | 2.07 | 83.0 |
| 8..... | 120 | 28.00 | 66.5 | 2.00 | 3.05 | 90.0 |
| 9..... | 144 | 28.48 | 75.83 | 1.13 | 4.56 | 80.0 |
| 10..... | 168 | 23.75 | 70.13 | 1.15 | 4.97 | 67.0 |
| 11..... | 192 | 23.59 | 69.88 | 2.38 | 4.95 | 65.0 |

There is here a marked difference in the quantitative relations of the various gases according, apparently, to the age of the culture. Charting these results, Plate I, we get a curve which at the end of thirty-six hours shows a maximum quantity of carbon dioxide. Seventy-two hours shows a decrease in carbon dioxide with a corresponding gain in hydrogen. During both of these periods the nitrogen and methane increase slowly but steadily, and are about equal in amount, the only exception being No. 5, eighty-four hours, in which there is a marked absence of both these gases. The third period is marked by a second rise in the amount of carbon dioxide, which is, however, slight, the hydrogen remaining about stationary. The methane now falls behind but the nitrogen is increased, an increase which is maintained in the last period, though here the carbon dioxide is reduced to a minimum and the hydrogen rises to a maximum.

Uniting the series under Table III, and Table IV, we get Tables VI and VII (Plate II and III), where we find that the same principle holds good, though the length of time occupied by the different stages is not exactly the same in all cases.

TABLE VI.

| No. | Duration of experiment. Hours. | Carbon dioxide. Per cent. | Hydrogen. Per cent. | Methane. Per cent. | Nitrogen. Per cent. | Total volume. cc. |
|---|---|---|---|---|---|---|
| 1 | 24 | 34.80 | 65.11 | .... | 0.09 | 100.0 |
| 2 | 46 | 35.58 | 60.34 | 1.34 | 2.74 | 97.8 |
| 3 | 48 | 30.2 | 62.83 | 1.63 | 5.34 | 97.4 |
| 4 | 84 | 32.27 | 61.39 | 1.80 | 4.54 | 94.8 |
| 5 | 120 | 28.11 | 64.6 | 1.80 | 5.49 | 86.8 |
| 6 | 140 | 30.00 | 62.72 | 1.78 | 5.50 | 98.0 |
| 7 | 144 | 30.41 | 62.88 | 1.77 | 4.94 | 96.0 |

TABLE VII.

| No. | Duration of experiment. Hours. | Carbon dioxide. Per cent. | Hydrogen. Per cent. | Methane. Per cent. | Nitrogen. Per cent. | Total volume. cc. |
|---|---|---|---|---|---|---|
| 1 | 24 | 33.41 | 64.07 | .... | 2.52 | 52.2 |
| 2 | 46 | 31.80 | 62.33 | 1.93 | 3.94 | 47.6 |
| 3 | 48 | 25.77 | 64.98 | 2.00 | 7.25 | 50.00 |
| 4 | 72 | 24.16 | 68.60 | 2.18 | 5.06 | 57.00 |
| 5 | 84 | 31.06 | 60.33 | 2.77 | 5.84 | 39.6 |
| 6 | 120 | 24.89 | 67.36 | 2.35 | 5.40 | 53.00 |
| 7 | 140 | 23.15 | 67.69 | 2.60 | 6.56 | 50.00 |
| 8 | 164 | 22.69 | 69.10 | 3.10 | 5.11 | 57.6 |

There seems to be, on the whole, an intimate relation between the reducing power which liberates hydrogen and that which liberates nitrogen. Carbon dioxide is generated in greatest quantity at the outset, when, perhaps, the available oxygen is most plentiful and poisonous waste products are in smallest proportion. The reducing power gains strength in the latter stages, when the conditions for carbon dioxide production are not favorable. If, as some investigators maintain, the denitrifying ability of *Bacillus coli communis* is due to a secondary action rather than to a primary one, the rise in carbon dioxide after gas production has been maintained for some hours may be accounted for on the supposition that those substances produced by the organism which liberate nitrogen have, through the reaction involved in that liberation, been so altered that their toxicity for the bacteria is, in part at least, removed. The carbon dioxide function then asserts itself, producing again products which are hurtful. These, combined with those already present, resolutely check the liberation of carbon dioxide. The hydrogen-producing function, as well as the nitrogen, can still maintain its existence for a time, thereby raising the relative proportions of those gases.

We believe that the irregularity of the foregoing results, even when made with the greatest care that we could bestow, is worthy of consideration. For the very great majority of these variations we can offer no definite explanations. It seems to us that refinement in manipulation brings to view variations which can only be due to life conditions, to cope with which our methods are incalculably clumsy. Until these methods are improved the quantitative chemistry of the living cell cannot progress very far, and it is with the plea for further work along these lines that this communication is made.

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# THE ADULTERATION AND ANALYSIS OF THE ARSENICAL INSECTICIDES.

BY J. K. HAYWOOD.

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IN the following paper I will first give a résumé of what has been done in the analysis of insecticides, showing which are usually pure and which often adulterated, and laying particular stress on the arsenical insecticides, which are of the most importance now on the market. This will be followed by a series of carefully-tested methods for the analysis of the more common insecticides, with the results indicated.

Various groups of insects act harmfully on plants and require special methods of treatment to kill them. Among these classes of insects may be mentioned subterranean insects, household pests, animal parasites, internal feeders, etc. The insects which principally injure plants, however, and for which insecticides are usually applied, are external feeders, which include "biting" and "sucking" insects.

For the first, or "biting" insects, some substance is used which can be sprayed on the parts of the tree attacked, and then eaten by the insect with its food. Such substances are Paris green, Scheele green, London purple, lead arsenate and arsenite, barium arsenite, arsenious oxide, etc.

For the second group, or "sucking" insects, substances must be used which will act externally on the bodies of the insects and smother them either by closing their pores or filling the air around with poisonous vapors. Among the latter insecticides may be mentioned insect powder, sulphur, kerosene, hydrocyanic acid, carbon disulphide, ammonia, formalin, etc. Experience has proved that a great many of the insecticides mentioned above are nearly always pure as they occur in commerce. There are certain ones, however, which often show adulteration, among them being cupric carbonate (impure because of faulty methods of manufacture), potassium cyanide, potash lye (which is often sodium hydroxide), formalin (which should be a 40 per cent. solution of formaldehyde, but often is not), and most of the arsenical preparations.

I will not attempt to go into the adulteration of all the articles mentioned above, but will lay particular stress on the adulteration of the arsenicals. These include Paris green, Scheele green, London purple, arsenious oxide, lead arsenate, white arsenoid, pink arsenoid, green arsenoid, paragrene, etc.

Paris green is supposed to be copper acetoarsenite and to contain 31.29 per cent. copper oxide, 58.65 per cent. arsenious oxide, and 10.06 per cent. acetic acid.

Scheele green is supposed to be copper hydrogen-arsenite and to contain 42.37 per cent. copper oxide, 52.32 per cent. arsenious oxide, and 4.81 per cent. water.

London purple is a by-product in the manufacture of the aniline dyes and is thought to be composed mainly of calcium arsenite with some coloring impurity, mostly rosaniline arsenite.

Besides London purple there are two other preparations, Paris and English purple, which have practically the same composition.

Of course arsenious oxide should be nearly pure, but in the crude state it may contain from 8 to 10 per cent. of cinders and other impurities.

White arsenoid is supposed to be barium arsenite; pink arsenoid is supposed to be lead arsenite; and green arsenoid is supposed to be copper arsenite.

Paragrene is a patented article which is said to be free from the objectionable features of Paris green, in that it never scorches the foliage.

Excepting the arsenious oxide, all of the above preparations may be, and often are, adulterated in one of three ways:

1. Some colored substance may be used to represent the compound, which will contain none of the elements which should be in the true compound. For example, samples have been analyzed which were labeled Paris green, but which contained neither arsenious oxide nor copper. Such imitations are usually harmless to the plant, but are equally harmless to the insect. Such a fraud as the above was noticed at the Alabama Station,[1] where a sample, called Paris green, was found to be composed of Prussian blue, chrome-yellow, and some inert substance, such as clay or chalk.

[1] Bulletin No. 58.

2. Some substance or substances may be added to the insecticides to increase their weight or to change their color, for use in making pigments. For example, Paris green is often adulterated with calcium sulphate, calcium carbonate, lead chromate, etc. This second form of adulteration is practiced more often in Germany than in America.

3. There may be arsenical insecticides containing a low per cent. of arsenious oxide in combination. It will be noticed that I say in combination. Many of the insecticides contain enough arsenic to include them in the class of high-grade articles, but this arsenic is often not in combination as it should be, but present as free arsenious oxide, thus forming a substance which will scorch the foliage of the tree.

The last of these three forms of adulteration is the most common in America, and must be considered as a fraud when we remember that free arsenious oxide not only scorches the foliage, but is usually much cheaper than the compound, which ought to be present. Sometimes it appears that the free arsenious oxide is added purposely; sometimes it is free because of faulty methods of manufacture.

Paris green, or copper acetoarsenite, has been repeatedly analyzed at the New Jersey Argricultural Experiment Station,[1] and has been found to range in percentage of arsenious oxide from 41.54 to 68.59 per cent. The excessively high percentage of arsenious oxide indicates that this cheaper substance had been added to the Paris green. Again, a sample of Paris green has been recently analyzed at the California Agricultural Experiment Station,[2] which contained 31.25 per cent. copper oxide and 52.90 per cent. arsenious oxide, but 23.60 per cent. of arsenious oxide, or nearly one-half, was in the free state. There were, besides, small amounts of impurities, including lime, soda, silica, sulphur trioxide, zinc oxide, etc. This most likely represents a sample where faulty methods of manufacture were used.

Another sample of Paris green, analyzed at the New Hampshire Station,[3] was found to have the following composition:

[1] Report, 1897, pages 397-492.
[2] Bulletin No. 126.
[3] Bulletin No. 43.

| | Per cent. |
|---|---|
| Arsenious oxide (does not say whether free or combined) | 30.00 |
| Insoluble in hydrochloric acid | 43.30 |

This insoluble portion was composed mainly of silica and oxides of iron and alumina, thus indicating that clay was the adulterant used.

Again at the Massachusetts Hatch Experiment Station,[1] two samples of so-called pure Paris greens were analyzed, which, not including various small amounts of impurities, had the following compositions:

| | Per cent. | Per cent. |
|---|---|---|
| Water at 100° | 5.00 | 4.29 |
| Arsenious oxide | 58.44 | 63.98 |
| Copper oxide | 8.30 | 6.60 |
| Calcium oxide | 14.50 | 15.98 |
| Sulphur trioxide | 7.56 | 5.80 |

The above analyses, of course, show adulteration with calcium sulphate. Samples of Paris green analyzed in Germany have been found to contain calcium sulphate, barium sulphate, lead chromate, lead sulphate, calcium carbonate, etc. One especially contained 25 per cent. of barium sulphate and 6.56 per cent. of lead chromate.[2]

As to Scheele green, the same adulterants are found as in Paris green. In a sample which I have just analyzed, the arsenious oxide and copper oxide appear in nearly theoretical proportions, but 17 per cent. of the arsenious oxide is in the free condition, thus making the sample worthless, unless previously treated with lime.

As to London purple, a sample analyzed at the New Jersey Station showed the following composition:

| | Per cent. |
|---|---|
| Water | 3.27 |
| Arsenious oxide | 41.44 |
| Calcium oxide | 24.32 |
| Alumina and iron | 3.37 |
| Sulphur trioxide | 0.31 |
| Dye by difference | 27.97 |

The arsenic in this sample was found to be present in the form $Ca_3(AsO_3)_2$, or the normal arsenite, but about 15 per cent.

[1] Bulletin No. 38.

[2] Stillman: *Chem. News*, 80, Nos. 20,087 and 20,088.

was soluble; therefore, although this sample was not adulterated, the analysis shows very careless making, as the manufacturers could just as easily have boiled with enough lime in the beginning. The process of manufacture, by the way, is to boil a waste product consisting of dye and arsenious oxide with lime, to make the insoluble calcium arsenite. Samples of London purple have been analyzed at the Cornell Station,[1] South Carolina Station,[2] the Florida Station,[3] and elsewhere, and wherever soluble arsenious oxide was determined it was found to be present in large amounts. It will also be easily seen that, owing to the intense color of London purple, various substances might be added to increase the weight without being perceptible to the naked eye.

White arsenoid, which is supposed to be barium arsenite, has recently been analyzed at the California Station[4] and found to possess the following composition:

| | Per cent. |
|---|---|
| Barium carbonate | 44.05 |
| Barium chloride | 13.05 |
| Barium oxide | 8.18 |
| Arsenious oxide, free | 27.64 |
| Lead carbonate | 1.86 |
| Silica | 0.20 |
| Water | 4.00 |

It will be seen that the only substance giving to this preparation any value as an insecticide is arsenious oxide, and since this is in the free state, it is harmful to the foliage. The barium salts are present only to give weight.

Pink arsenoid is supposed to be lead arsenite. A recent analysis made at the California Agricultural Experiment Station[4] showed that it had the following composition:

| | Per cent. |
|---|---|
| Lead oxide | 49.58 |
| Arsenious oxide, combined | 40.02 |
| Arsenious oxide, free | 3.24 |
| Water | 0.31 |
| Organic matter from aniline residue and lead sulphate | 6.85 |

[1] Bulletin No. 18.
[2] S. C. Report, 1888, page 142.
[3] Florida Station Bulletin No. 14.
[4] Bulletin No. 126.

This preparation is evidently unadulterated and has given very good results.

Green arsenoid, or copper arsenite, analyzed at the California Station,[1] showed the following composition:

| | Per cent. |
|---|---|
| Arsenious oxide | 61.33 |
| Copper oxide | 28.83 |
| Water | 2.77 |
| Silica | 0.40 |
| Organic material, sodium sulphate, etc. | 6.67 |

7.82 per cent. of this arsenious oxide was soluble.

Paragrene has also recently been analyzed at the California Station and found to owe its poisonous properties mainly to arsenious acid and copper oxide. It contains 23.46 per cent. copper oxide and 40.60 per cent. of arsenious oxide, but 23.08 per cent. of this is free. It also contains 19.31 per cent. of gypsum to add weight. The preparation is therefore harmful to the plant.

In the Canada Experimental Farm Report of 1895, page 220, mention is made of lead arsenate. This substance is obtained by the action of sodium arsenate on lead acetate. It is there stated that there is no reason lead arsenate so manufactured should contain impurities, but that it often does, however, because of the original impurities in the sodium acetate, a by-product obtained in the manufacture of aniline dyes.

Arsenious oxide, because of its method of preparation, may, in the crude state, contain from 2 to 10 per cent. of arsenious sulphide and ore dust as impurities, it being usually prepared by roasting mispickel or tin ores.

I must not leave this subject without calling attention to two insecticides, called respectively "Peroxide of Silicates" and "Hammond's Slug Shot." The first, on analysis at the Vermont Station,[2] was shown to have the following composition:

| | Per cent. |
|---|---|
| Water | 1.44 |
| Arsenious oxide | 1.47 |
| Copper oxide | 0.28 |
| Lime | 36.43 |
| Sulphur trioxide | 52.29 |
| Ferric oxide and aluminum oxide | 1.40 |
| Sand | 1.93 |
| Organic and volatile matter | 4.76 |

[1] Bulletin No. 126.

[2] Bulletin No. 12.

It is needless to say that this sample, composed mostly of calcium sulphate, did not give good results.

"Hammond's Slug Shot," by an analysis made at the Vermont Experiment Station,[1] was shown to have the following composition:

| | Per cent. |
|---|---|
| Water of hydration | 14.76 |
| Arsenious oxide | 1.58 |
| Cupric oxide | 0.60 |
| Lime | 30.24 |
| Sulphur trioxide | 43.02 |
| Ferric oxide and aluminum oxide | 0.79 |
| Sodium chloride | 2.83 |
| Insoluble | 1.38 |
| Organic and volatile matter (mostly dead oil by difference) | 4.79 |

Here again it will be seen that in buying the above substance one is paying a pretty good price for an article composed almost entirely of calcium sulphate.

I have gathered together a bibliography of the arsenical insecticides, of which the examples presented above form only a small fraction. These are, however, fairly representative of the different classes of adulterants.

## ANALYSIS OF INSECTICIDES.

### (Paris green and Scheele green.)

Recently it became necessary for me to make analyses of various arsenical insecticides, but on looking up the matter I found that few good methods had been published. Many of the Stations had partially analyzed these substances, but even the methods employed in these partial analyses were not given. I therefore decided to test some of the few more promising methods which are known, and where methods were not known, try to work them out on the following substances: Paris green, Scheele green, London purple, and white arsenic.

An analysis of Paris green would include determinations of total and soluble arsenious oxide, copper oxide, moisture, acetic acid, and matter insoluble in dilute hydrochloric acid. An analysis of Scheele green would include determinations of all the substances named above, except acetic acid. An analysis

[1] Bulletin No. 12.

of white arsenic would, of course, include only the determinations of water and total arsenious oxide to ascertain the purity.

A determination of the moisture in Paris green is made in the usual way by drying for twelve to fifteen hours, at the temperature of boiling water. On two samples the results were:

| | A. Per cent. | B. Per cent. |
|---|---|---|
| Moisture | 1.30 | 0.99 |

1. For a determination of the total arsenious oxide, I first tried the well-known method, as given by Fresenius, of dissolving in hydrochloric acid, oxidizing to arsenic acid with potassium chlorate, driving off the chlorine at a gentle heat, making ammoniacal, precipitating with magnesia mixture, filtering and washing in a Gooch crucible, putting a cap on the crucible drying first at 100° and then at 130° C., heating on a sand-bath, then on an iron plate, and finally heating over the blast-lamp and weighing as magnesium pyroarsenate. This method, however, in the first place, is very long because of the time taken in getting rid of the chlorine and in igniting the precipitate by degrees; secondly, there is great danger of loss of the arsenic, as arsenious chloride; and thirdly, the precipitate of ammonium magnesium arsenate is somewhat soluble in the ammonia wash and has not quite the theoretical composition. After obtaining rather varying results, this method was abandoned.

2. I next tried to determine the arsenic by the following method: Oxidize the Paris green in a small flask, closed with a funnel on the steam-bath, by means of fuming nitric acid. Pour out in a dish and evaporate to dryness; take up with hydrochloric acid and proceed as in the first method, finally weighing the arsenic as magnesium pyroarsenate. This plan shortens the time necessary to determine the arsenic and rids one of the danger of loss as arsenious chloride, but there is still present the third source of error, mentioned above. Proceeding in this way, I obtained the following results on two samples of Paris green ("A and B"), and on a sample of dry, chemically pure arsenious oxide:[1]

[1] In every case where the arsenic was weighed as magnesium pyroarsenate, a correction was made of 0.0008 gram magnesium pyroarsenate, for each 30 cc. of ammoniacal filtrate containing an excess of magnesium mixture as suggested by Fresenius.

| | Arsenious oxide. Per cent. |
|---|---|
| Paris green, "A" | 56.03<br>56.03 |
| Paris green, "B" | 56.68<br>56.69 |
| Arsenious oxide, C. P | 99.33<br>99.18 |

3. I next tried a method suggested by Thorn Smith.[1] As described by himself, the method is as follows:

"Two grams of Paris green are weighed out and about 100 cc. of water and 2 grams of sodium hydroxide added. The solution is brought to a boil and the boiling is continued for a few minutes (thus precipitating copper as cuprous oxide). It is then allowed to cool to room temperature and the solution made to 250 cc. The well-shaken liquid is filtered through a dry filter and 50 cc. taken for analysis. This portion is concentrated to about one-half of its volume and allowed to cool to about 80° C. An equal volume of strong hydrochloric acid is then added, accompanied by 3 grams of potassium iodide, and the whole allowed to stand for ten minutes (to reduce the arsenic oxide to arsenious oxide). The deep red solution is slightly diluted with water to dissolve the precipitate caused by the potassium iodide, and a dilute solution of sodium hyposulphite added, until the color just disappears. This solution is then made neutral by the addition of dry sodium carbonate and finally an excess of sodium bicarbonate is added. Tenth normal iodine is dropped in and the end reaction noted by the starch solution."

In applying this method, I used one or two precautions, not mentioned by Smith; namely, instead of making neutral with dry sodium carbonate and very likely getting in an excess, I added dry sodium carbonate until the bubbles came off slowly, showing that the acid was really neutralized, and then sodium bicarbonate to neutrality and some in excess. This was done, because if any free sodium carbonate is present it will itself act on the iodine solution. Again, after using up the iodine which was set free in reducing the arsenic to arsenious oxide by sodium hyposulphite, the solution was immediately diluted, since the air

[1] This Journal, 21, 769.

is apt to act on the hot, concentrated solution of hydriodic acid and set free some iodine if this is not done.[1]

On applying this method to the two samples of Paris green ("A" and "B") and the dry, chemically pure arsenious oxide the following results were obtained:

| | Arsenious oxide. Per cent. |
|---|---|
| Paris green "A" | 56.85<br>56.96 |
| Paris green "B" | 57.63<br>57.45 |
| Arsenious oxide, C. P.[2] | 100.10<br>100.10<br>99.86 |

It will not be out of place here to speak of the standardization of the iodine solution, since it is upon the correctness of this standardization that the accuracy of the above method depends. A great many text-books give the following method for standardizing the iodine solution:

Weigh out a small portion of dry, chemically pure arsenious oxide, dissolve in sodium hydroxide, make slightly acid with hydrochloric acid, and then add an excess of sodium bicarbonate. Run in the iodine solution, using starch as an indicator, until the blue color appears.

I used this method of standardizing at first, but it soon seemed to me that perhaps it was not correct, since the literature on the subject speaks of the alkali arsenites being partially oxidized to the "arsenates" upon boiling the solution, exposed to the air. I therefore used a dry, chemically pure portion of arsenious oxide and carried it through by the Thorn Smith method, standardizing my iodine solution against the arsenious oxide, as finally reduced by potassium iodide. In every case, I found that on adding potassium iodide to the hydrochloric acid solution of the arsenite some iodine was set free, showing that a small amount of arsenate had been formed, which should be reduced before running in the iodine solution.

Applying these two methods to an approximately tenth-normal

[1] Gooch and Browning: *Am. J. Sci.*, **40**, 66 (1890).

[2] The iodine solution for the determination of arsenic trioxide in the chemically pure arsenic trioxide was not standardized against arsenious oxide, but against sodium hyposulphite, which had in turn been standardized against the amount of iodine set free, when potassium iodide acts on a weighed quantity of potassium dichromate in the presence of hydrochloric acid.

iodine solution, I obtained by the old method of standardization 1 cc. iodine solution = 0.012607 gram iodine, and by the Smith method of standardization 1 cc. iodine solution = 0.012484 gram iodine. It will at once be seen that the errors caused by the sodium arsenite partially oxidizing to sodium arsenate is larger than should be allowed in a standard solution.

A determination of the copper oxide in Paris green was made in the following well-known manner:

The cuprous oxide obtained in the Thorn Smith method by boiling the Paris green with sodium hydroxide was poured on the filter (after taking an aliquot portion of the solution for the determination of arsenious oxide) and well washed with hot water. It was then dissolved with hot dilute nitric acid and made to a volume of 250 cc., one-fifth being taken for analysis. The copper in solution was determined either by means of the galvanic current or, when that was not handy, in the following manner:

The nitric acid solution was made alkaline with sodium carbonate, then made slightly acid with acetic acid, and about ten times the weight of the copper in potassium iodide added. When it was all dissolved, the free iodine was titrated with a standard solution of sodium hyposulphite, using starch as indicator. The full details of this method are given in Sutton's "Volumetric Analysis," third edition, page 133. The results on the two samples of Paris green by this method were as follows:

| | Cupric oxide. Per cent. |
|---|---|
| Paris green "A" | 29.79<br>30.37<br>30.15 |
| Paris green "B" | 29.79<br>29.79<br>29.79 |

The figure for acetic acid in Paris green is usually obtained by subtracting the sum of total arsenious oxide, water, cupric oxide, and residue left after treating with dilute hydrochloric acid, from 100.

As to the determination of soluble arsenic in Paris green, I could find very little in the literature on the subject which was of any value. I therefore tried several schemes:

1. I weighed 1 gram of Paris green on a filter-paper and washed it with cold water. Each time 200 cc. were obtained, sodium bicarbonate was added and the solution titrated with iodine solution. After about 2,000 cc. of wash liquor had been used the filtrate was still slowly gaining in arsenious oxide. The method was therefore abandoned as impracticable.

2. I weighed out several 1-gram samples of Paris green and treated these in flasks with 500 cc. of water. The flasks were stoppered and occasionally shaken each day. Every few days an aliquot portion of 100 cc. was filtered off from one of the flasks and the arsenious oxide titrated with iodine after the addition of sodium bicarbonate. The results on the samples of Paris green ("A" and "B") were as follows:

| | Time. Days. | Arsenious oxide extracted. Per cent. |
|---|---|---|
| Paris green "A" | 2 | 1.01 |
| " " " | 4 | 1.68 |
| " " " | 8 | 2.69 |
| " " " | 11 | 4.02 |
| " " " | 14 | 4.02 |
| " " "B" | 9 | 3.41 |
| " " " | 12 | 4.86 |
| " " " | 14 | 4.86 |

It will thus be seen that this method finally gave constant and very likely correct results. It is rather long, but very little attention or time had to be given after the first weighing out.

3. To expedite matters, I next tried the following method for determining the soluble arsenious oxide. One-half gram of Paris green was weighed out, placed in a flask and treated with about 200 cc. of water. This was digested with occasional shaking on the water-bath at 50° to 60° C., and each day all of the water poured off through a filter, and, after returning all of the substance from the filter to the flask, a fresh portion of water was added and the digestion continued. The arsenious oxide was determined by means of a standard iodine solution. The results on the samples of Paris green ("A" and "B") were as follows:

| | Time. Days. | Arsenious oxide extracted. Per cent. |
|---|---|---|
| Paris green "A" | 1 | 3.41 |
| " " " | 2 | 3.41 + 2.14 = 5.55 |
| " " " | 3 | 5.55 + 1.56 = 7.11 |
| " " " | 4 | 7.11 + 1.17 = 8.28 |
| " " " | 5 | 8.28 + 1.26 = 9.54 |
| " " " | 6 | 9.54 + 1.56 = 11.10 |
| " " " | 7 | Still gaining. |
| " " "B" | 1 | 2.24 |
| " " " | 2 | 2.24 + 1.46 = 3.70 |
| " " " | 3 | 3.70 + 1.26 = 4.96 |
| " " " | 4 | 4.96 + 1.17 = 6.13 |
| " " " | 5 | 6.13 + 1.17 = 7.30 |
| " " " | 6 | 7.30 + 1.56 = 8.86 |
| " " " | 7 | Still gaining. |

It will thus be seen that a hot extraction can not be used, since the Paris green either breaks up or goes into solution in the presence of hot water, the amount of arsenious oxide going into solution each day being finally nearly constant.

The same methods for determining the constituents of Scheele green were used as those for Paris green mentioned above. On one sample the moisture was 5.27 per cent.

The total arsenious oxide was as follows:

By Method 1. Oxidation with HCl and $KClO_3$ ..... Not tried

By Method 2. Oxidation with $HNO_3$ ..... { 50.63 / 50.80

By Method 3. Thorn Smith ..... { 51.39 / 51.27

The determination of the cupric oxide by the method mentioned above gave the following results:

Cupric oxide ..... { 38.04 / 38.23

The soluble arsenious oxide determination gave the following results by the various methods:

1. Washing on filter. Not tried.
2. Extracting with 500 cc. cold water:

| Time. Days. | Arsenious oxide extracted. Per cent. |
|---|---|
| 6 | 13.09 |
| 9 | 14.30 |
| 13 | 16.26 |
| 21 | 16.73 |
| 34 | 17.82 |
| 36 | 17.70 |

3. Extracting with water at 50° to 60° C.:

| Time. Days. | Arsenious oxide extracted. Per cent. |
|---|---|
| 1 | 13.43 |
| 2 | 13.43 + 3.70 = 17.13 |
| 3 | 17.13 + 1.85 = 18.98 |
| 4 | 18.98 + 0.87 = 19.85 |
| 5 | 19.85 + 0.78 = 20.63 |
| 6 | 20.63 + 0.58 = 21.21 |
| 7 | 21.21 + 0.49 = 21.70 |
| 8 | 21.70 + 0.39 = 22.09 |
| 9 | 22.09 + 0.39 = 22.48 |
| 10 | 22.48 + 0.39 = 22.87 |
| 11 | Still gaining. |

From the above work I would draw the following conclusions:

1. Water can be determined in Paris green and Scheele green by drying at the temperature of boiling water for twelve to fifteen hours.

2. The best method for determining the total arsenious oxide in Paris and Scheele greens is the Thorn Smith method, marked 3 above.

3. The best method for determining the soluble arsenious oxide in Paris and Scheele greens is by extracting with 500 cc. of water at room temperature.

4. Hot water extraction can not be used to extract soluble arsenious oxide.

5. A good method for determining copper in Paris and Scheele greens is the volumetric method based on the titration of the iodine set free from potassium iodide by a copper salt in acetic acid solution.

Appended is a condensed statement of the work done:

| | | Total arsenic. | | |
|---|---|---|---|---|
| | Water. Per cent. | Oxidation with potassium chlorate. | Oxidation with nitric acid. Per cent. | Method of Smith. Per cent. |
| Paris green "A" | 1.30 | Abandoned | 56.03 | 56.90 |
| Paris green "B" | 0.99 | " | 56.69 | 57.54 |
| Scheele green | 5.27 | " | 50.66 | 51.33 |
| Arsenious oxide, C. P. | None | " | 99.25 | 100.02 |

| | Soluble arsenious oxide. | | | | |
|---|---|---|---|---|---|
| | Wash on filter. | 500 cc. cold water. Per cent. | Water at 50°–60° C. | Cupric oxide. Per cent. | Insoluble in hydrochloric acid. |
| Paris green "A"..... | Abandoned | 4.02 | 11.10+ | 30.07 | None |
| Paris green "B"..... | " | 4.86 | 8.86+ | 29.79 | None |
| Scheele green..... .. | " | 17.76 | 22.87+ | 38.14 | None |
| Arsenious oxide, C. P. | .... | .... | .... | .... | None |

A continuation of this paper will appear during the next few months, which will have for its object the creation and improvement of the methods of estimating the various constituents of London purple as well as a study of the improved method of estimating arsenic gravimetrically by Martha Austin,[1] which has only come to my notice since the above work was completed.

## THE DETECTION OF COAL-TAR DYES IN FRUIT PRODUCTS.

By A. L. Winton.

Received July 5, 1900.

SOON after its discovery fuchsine came into use for coloring wines and replaced to a large extent the vegetable dyes which from very early times had been employed for this purpose. More recently various other coal-tar dyes, particularly the azo-colors, have been extensively used in wines although fuchsine and acid fuchsine are still preferred by some makers.

Within the past few years the use of coal-tar dyes in articles of diet has attracted the attention of food analysts in the United States. In the case of confectionery, pastries, and some other products they serve merely to render the articles more attractive to the eye without deceiving the purchaser, but as a rule they give imitation products the appearance of the genuine or, to use the legal phraseology, "they make the products appear better or of greater value than they really are."

Some of the results obtained by Winton, Ogden, and Mitchell, in the examination of foods at the Connecticut Agricultural Experiment Station, illustrate the fraudulent use of dyes. In 1898, sixty-three samples of jellies purporting to have been made from fruit were examined, and of these, twenty-eight were spurious mixtures colored with coal-tar dyes. Some of the most remarkable samples, labeled "strawberry jelly," "raspberry

1 *Ztschr. anal. Chem.*, 23, heft 2.

jelly," etc., consisted of starch paste, flavored with artificial "fruit ethers," sweetened with glucose and preserved with salicylic acid, the dye having been used to carry out the deception. Of twenty-eight samples of fruit preserves, eight were also colored with coal-tar dyes. During the following year (1899) ninety-two samples of soda-water sirups, chiefly strawberry, raspberry, and orange, were subjected to analysis. Of these, forty-five were colored with coal-tar dyes. As a rule the sirups which were artificially colored were also artificially flavored and contained no genuine fruit juice whatever. Dyes were also found in bottled carbonated beverages.

The relation of these dyes to public health deserves attention. The experiments carried on with dogs and other animals by Cazeneuve and Lépine, Weyl, and others have proved beyond a doubt the poisonous nature of picric acid, dinitrocresol, and Martius' yellow, among the nitro-colors, and of orange II and metanil yellow among the azo-colors. Fuchsine, sulphonated nitro-colors, and most of the azo-colors did not act as poisons although some of the azo-colors produced vomiting, others diarrhea, and many developed slight albuminuria.[1]

Although there is evidence that the bulk of the coal-tar dyes are not injurious to some of the lower animals, it is not safe to assume that they are entirely harmless to human beings. The dog, the animal used in most of Weyl's experiments, has a proverbially strong stomach and eats, with no apparent discomfort, many things which would disturb the digestion of a man.

The unwholesomeness of certain coal-tar dyes not classed as poisons is indicated by the experience of Weber[2] who tested their effect on the artificial digestion of fibrin with pepsin and with pancreatin. He found that oroline yellow (acid yellow) retarded the action of pepsin and that methyl orange, saffoline (acridine red), and magenta (fuchsine) seriously interfered with the pancreatic digestion. Of these, fuchsine, at least when pure, had been pronounced entirely harmless by earlier investigators who based their conclusions on experiments with lower animals and some few with man.

[1] "The Coal-tar Colors" by Theodore Weyl, translated by Henry Leffmann, pp. 54-148.
[2] This Journal, 18, 1092.

Even if the entire harmlessness of most of the coal-tar dyes is conceded, in view of the injurious properties of some of them and the difficulty of distinguishing these from the harmless dyes when present in food products, the safe course is to exclude all dyes of coal-tar origin from articles of diet. In Austria their use is entirely prohibited and in other countries they are regarded with suspicion.

In carrying out the work of food examination under adulteration laws the analyst is often called upon to determine whether or not a coal-tar dye is present, if not to identify the particular dye.

Numerous methods of testing wines for these dyes are described in the journals and in the works on food analysis but almost nothing has been published on their detection in jellies, preserves, fruit sirups, and other fruit products.

Because of the absence of special methods I have adapted some methods originally devised for wines for use in testing other products and publish the following details, with precautions learned by experience, for the benefit of others engaged in similar work.

In applying these tests to jellies and other semisolid products it is necessary to bring into solution by boiling with 1 to 5 parts of water.

### ARATA'S WOOL TEST.[1]

One hundred cc. of the liquid to be tested, prepared if necessary as described in the preceding paragraph, are boiled for ten minutes with 10 cc. of 10 per cent. solution of potassium bisulphate and a piece of white wool, or woolen cloth, which has been previously heated to boiling in a very dilute solution of sodium hydroxide and thoroughly washed in water. After removal from the solution, the wool is again washed in boiling water and dried between pieces of filter-paper. If the coloring-matters are entirely from fruit, the wool either remains uncolored, or takes on a faint pink or a brown color which is changed to green by ammonia and is not restored by washing in water; but if certain coal-tar dyes, chiefly of the azo-group, are present,

[1] *Ztschr. anal. Chem.* **28**, 639. See also Borgman: "Anleitung chem. Anal. d. Weines," Wiesbaden, 1898, p. 91. Koenig: "Untersuchung landw. u. gewerb. wich. Stoffe," Berlin, 1898, 577.

the wool is dyed and the color on the fibers is either not changed by ammonia or, if changed, is restored by washing.

The dye present may often be identified by noting the color of the wool after addition of enough concentrated sulphuric acid to thoroughly moisten the fibers and again after dilution of the acid.[1] As a rule it is not desirable to proceed further with the test although Arata gives instructions for removing the dye from the wool and testing the dye itself. For this purpose the wool is treated with dilute tartaric acid solution to remove vegetable colors, washed in water and dried between sheets of filter-paper. It is then transferred to a test-tube and saturated with concentrated sulphuric acid. After standing five or ten minutes, water sufficient to make 10 cc. is added and the wool is removed. The solution after making alkaline with ammonia and cooling is shaken with 5 to 10 cc. of pure amyl alcohol, to which a few drops of ethyl alcohol are added, to facilitate the separation. The alcoholic extract is separated, evaporated to dryness, and the residue tested according to the scheme of Girard and Dupré, Witt,[2] Weingaertner[3] or Dommergue.[4]

I have applied this test to samples of juices, sirups, jellies, and preserves prepared in the laboratory from the fruits, as well as to numerous commercial fruit products including catsups. The woolen cloth used was "nun's veiling" cut into pieces one inch wide and three inches long.

When strawberry, raspberry, blackberry, currant, grape, and cherry juices, without dilution, were treated as has been described, the wool acquired a dull pink or brownish pink color. With ammonia the color changed to green, and washing with water in no case restored the original color. Treatment with 10 per cent. tartaric acid solution in the cold was without effect, but on boiling for some time the pink color was largely removed. From orange, lemon, pineapple and tomato juice or pulp, the wool absorbed no color at all, or only a faint yellow color.

Jellies, preserves, sirups, and catsups known to be pure gave up to the wool very slight colors, but many of the commercial

[1] See scheme of Girard et Dupré: "Analyse des Matières Alimentaires et Recherche de leurs Falsifications."

[2] *Ztschr. anal. Chem.*, **26**, 100.

[3] *Ibid.*, **27**, 232.

[4] *Ibid.*, **29**, 369.

products imparted to the wool intense red, orange, magenta, and even green shades. Treated with ammonia, these bright colors remained unchanged or, if changed, washing restored the original color.

Boiling with tartaric acid solution also failed to affect the colors. By treatment with concentrated sulphuric acid and dilution of the acid, color reactions for acid fuchsine, tropæolins, ponceaus, Bordeaux red, eosins, and other dyes were obtained.

I have found it more satisfactory to test the dyed wool directly, rather than the color obtained from the wool as directed by Arata, because only a few dyes are extracted by amyl alcohol from alkaline solutions, and, as explained further on, tests of the residues left after evaporating the extracts are indecisive.

Care should be taken to determine whether the wool is dyed, or merely coated with the color. For example, chlorophyl from green coloring preparations of vegetable origin, is deposited on wool, together with fat and resin, but the color, unlike the coal-tar dyes, rubs off on the fingers and is readily washed out with soap and water.

For the purpose of illustrating the amount of artificial color present in each glass of adulterated carbonated beverages, I have employed 250 cc. portions of the beverages (or 40 to 50 cc. of sirups diluted to 250 cc.) and pieces of nun's veiling six inches square. The dyed squares thus obtained furnish striking object lessons. From strawberry, raspberry, cherry, and blood-orange flavors, brilliant red and magenta shades were fixed on the wool (acid magenta, Bordeaux red, ponceaus, etc.); from orange and lemon flavors, orange and yellow shades (tropæolins, etc.); and from mint preparations, bright green and yellow-green colors.

### AMYL ALCOHOL TEST, ALKALINE SOLUTION.[1]

Twenty-five cc. of the liquid to be tested, made alkaline with ammonia, are shaken cautiously for some minutes in a separatory funnel, with pure amyl alcohol. If the clear alcoholic layer, when separated from the aqueous solution, is colored, or if addition of acetic acid develops a magenta color (fuchsine), a portion of it, together with an equal bulk of water and a thread of

[1] "Analyse des Matières Alimentaires et Recherche de leur Falsifications", Par Girard et Dupré, pp. 167, 582.

wool, is heated on a water-bath, the water lost by evaporation being replaced from time to time.

The presence of a coal-tar dye should not be affirmed until the color has been fixed on wool and the wool has been washed in boiling water, dried, and tested with sulphuric acid. When fuchsine is present, the color which appears on adding acetic acid to the alcohol extract is changed to yellow by hydrochloric acid. Ether or ethyl acetate may be used in place of amyl alcohol for extracting fuchsine.

### AMYL ALCOHOL TEST, ACID SOLUTION.[1]

Twenty-five cc. of the liquid, to which have been added a few drops of hydrochloric acid, are shaken with amyl alcohol, and dyeing tests are made as described in the preceding section.

A colored amyl alcohol does not prove the presence of a coal-tar color, as I have found that red coloring-matters are extracted by this solvent from acid solutions of pure fruit juices. These solutions, however, do not dye wool, when treated as above described.

Some authors recommend that the sulphuric acid test be applied to the residue left after evaporating the amyl alcohol extract. This may be satisfactory in wine analysis but with fruit jellies, etc., this residue is liable to contain other organic matters which obscure the color reactions of coal-tar dyes.

If amyl alcohol extracts from the liquid, after acidifying, an orange color which has not been found to be of coal-tar origin, test may be made for cochineal.

The alcohol is washed several times with water and divided into two portions. To one portion is added a solution of uranium acetate, drop by drop, with shaking. In the presence of cochineal the aqueous solution acquires an emerald-green color.[2] As a confirmatory test the other portion is made alkaline with ammonia which changes the orange color of cochineal to purple.

### GIRARD'S TEST FOR ACID FUCHSINE (ACID MAGENTA).[3]

If a bright magenta color is fixed on wool by Arata's test and

[1] "Analyse des Matières Alimentaires et Recherche der leur Falsifications," Par Girard et Dupré, p. 582.

[2] *Ibid.*, p. 580.

[3] *Ibid.*, p. 169.

if ordinary fuchsine has been proved to be absent, test should be made for acid fuchsine.

To 10 cc. of the liquid are added 2 cc. or more of 5 per cent. solution of potassium hydroxide. The strongly alkaline liquid is mixed with 4 cc. of 10 per cent. solution of mercuric acetate and filtered. The filtrate should be alkaline and colorless. If addition of a slight excess of dilute sulphuric acid produces a violet-red coloration and other dyes have not been found by the amyl alcohol test, the presence of acid fuchsine may be affirmed.

I have found this test useful in the examination of fruit juices and sirups but unsatisfactory in the case of jellies owing to difficulties in filtration and undecisive reactions.

### CAZENEUVE'S METHOD.

Cazeneuve's mercuric oxide method[1] for detection of coal-tar dyes which has been extensively employed in wine analysis did not prove satisfactory in the examination of jellies. This method, however, deserves trial with fruit juices and sirups, which are more easily handled than the gelatinous products.

In testing a suspected sample I apply first of all Arata's test. The other tests described are employed either to confirm the results obtained by Arata's test or to supply evidence in cases where that test fails.

The analyst should be extremely cautious in naming the particular dye present in a sample. It should be remembered that the number of coal-tar dyes on the market is exceedingly large and that new dyes are continually being introduced. A reaction which a few years ago may have been characteristic of a particular dye may to-day be common to several dyes. As a rule it is only necessary to learn whether or not a color is of coal-tar origin. In fact such terms as "red coal-tar dye" and "orange coal-tar dye" are often to be preferred in an official report to the cumbersome scientific names or the equally unintelligible commercial names.

CONNECTICUT AGRICULTURAL EXPERIMENT STATION,
NEW HAVEN, CONN., June, 1900.

[1] "Analyse des Matières Alimentaires et Recherche der leur Falsifications," Par Girard et Dupré, p. 174; *Compt. rend.*, 102, 52.

[CONTRIBUTION FROM THE DEPARTMENT OF FOOD AND DRUG INSPECTION OF THE MASSACHUSETTS STATE BOARD OF HEALTH.]

# ESTIMATION OF FAT IN CONDENSED MILK.

BY ALBERT E. LEACH.

Received July 9, 1900.

THE use of canned, sugar-preserved, condensed milk has increased considerably during the last few years, no less than forty brands of the article being on sale in Massachusetts at the present time. In view of the fact that of all its ingredients the fat is the only one that can be conveniently tampered with to produce an inferior or cheaper product, it becomes highly important to have at hand a ready and accurate means of fat determination, especially where samples have to be examined systematically and in large numbers for adulteration.

The Babcock centrifuge method, so convenient for estimating fat in ordinary milk, was long thought to be out of the question for use with sugar-preserved milk, by reason of the fact that the cane-sugar, which is present to the extent of some 40 per cent. in the average condensed milk, becomes so charred by the action of the sulphuric acid employed in the test as to produce nothing but a black mass in place of the desired column of clear fat. This has been the common experience of all who tried it.

The Adams-Soxhlet method, which is the recognized standard for fat determination in ordinary milk, has been largely used in the case of condensed milk, but, in the writer's experience, can not be depended on for the latter purpose, on account of the fact that the large amount of cane-sugar present, even when the sample is diluted for analysis, encloses the fat particles so firmly, when dried on the extraction coil, as to render its removal by the solvent ether a very difficult matter.

In 1895 the writer devised a scheme whereby the Babcock machine could be satisfactorily used for condensed milk fat, and an outline of the process as then carried out was published in the "Annual Report of the Massachusetts State Board of Health for 1896." This process, with certain minor modifications which experience has from time to time suggested, has been in successful use in the Food and Drug Department of the Board for over five years, and has proved itself to be not only much quicker

than the Adams-Soxhlet extraction method and easier of manipulation, but, indeed, more accurate, by reason of the fact that the cane-sugar with all its attendant troubles is first eliminated.

If, in the case of condensed milk, ordinary ether is used as a reagent for the Soxhlet extraction, the amount of extract weighed as fat may not *appear* too low, because the alcohol and water present in the ether dissolve not only fat, but also sugar, which goes in with, and is weighed as fat. On the contrary, if the ether be dehydrated with calcium chloride and distilled over sodium, to free it completely from alcohol, the extracted fat will be found to be far too small. The same incomplete extraction results from the use of benzine or petroleum ether as a solvent.

Parallel determinations of fat in sugar-preserved milk by the Adams-Soxhlet process, using ether carefully dehydrated and freed from alcohol, and by the writer's method involving the use of the Babcock machine, show in all cases a larger fat content by the latter or modified Babcock process. Indeed, in one instance an extraction of sixty hours was required in the case of the Soxhlet process to equal the percentage of fat found by the modified Babcock process, so firmly were the fat particles enclosed by the cane-sugar on the extraction coil, thus resisting the action of the ether. It is obvious that, in the case of the modified Babcock process, no more fat can be shown by the final result than actually exists in the milk; indeed, if anything, one would expect a slight loss, so that, when compared with the Soxhlet method, if the latter shows lower figures, it can safely be presumed that the process is unreliable. This, of course, applies only to the sugar-preserved variety of condensed milk.

The improved method of fat estimation with the Babcock centrifuge is as follows: Having first insured a homogeneous sample of the contents of the can by stirring, 40 grams are weighed out preferably in a weighing tray for sugar, transferred by washing to a graduated 100 cc. sugar flask, and made up to the mark with water. Twenty-five cc. of the thoroughly mixed diluted sample, corresponding to 10 grams of the original condensed milk, are measured by a pipette into an ordinary test-bottle of the Babcock centrifuge. This is filled nearly to the neck with water, and 4 cc. of a solution of copper sulphate of the strength of Fehling's copper solution are added. The contents are thor-

oughly shaken, and the precipitated proteids, carrying with them the fat, are rapidly separated out by whirling the fat bottle in the centrifuge, preferably (though not necessarily) without heating. The writer prefers an electric centrifuge of the Robinson type for this purpose, as the heat of the steam-driven machine cakes the precipitate down, so that it is harder to wash. If desired, the precipitate may be allowed to settle out of itself, which it does more quickly in the cold.

The supernatant liquid containing the sugar is drawn off by means of a pipette of large capacity, having a stem sufficiently small to pass easily into the neck of the milk bottle, a small wisp of absorbent cotton being first twisted over the bottom of the pipette to serve as a filter. If many samples are to be treated, a suction-pump, connected by rubber tubing with the pipette, is a great convenience. On withdrawing the pipette with the sugar solution, the cotton is wiped off into the bottle by rubbing against the inner side.

The precipitated proteids and fat are given two additional washings, as above, by shaking thoroughly with water introduced nearly to the neck of the bottle, separating out in each case by centrifuge or by settling, and finally removing the washings with the pipette, two of such extra washings being found nearly always sufficient to remove all the sugar. If the precipitate is caked down hard after treatment with the centrifuge, it may be necessary to employ a stiff platinum wire as a stirrer to aid in mixing with the wash-water.

Finally, enough water is added to amount approximately to the normal volume of 17.6 cc. usually employed for the Babcock test, 17.5 cc. of sulphuric acid are added, and the test continued from this point on as in the ordinary Babcock process of milk testing, multiplying the reading obtained by 1.8 to give the correct percentage of fat in the sample.

For condensed milk containing no added cane-sugar, these precautions are, of course, unnecessary, the ordinary Babcock method being directly employed with a weighed portion of the milk.

# ON CERTAIN PECULIARITIES IN THE URINE OF VEGETARIANS.

By J. H. Long.

Received July 23, 1900.

I HAVE recently presented the results of analyses of a number of normal urines[1] in which the relation of the copper oxide reducing power to the amounts of creatinin and uric acid present, was especially noted. In this paper I shall give briefly the corresponding data found by examining the urine of individuals living wholly on a vegetable diet. As the methods of examination were the same as formerly employed, it will not be necessary to refer to them again. The seven men who furnished the urine for the tests are students of the American Medical Missionary College of Battle Creek and Chicago, and for a year or longer had lived on a diet of bread, fruits, vegetables, and prepared cereal and nut foods exclusively. Eggs were not eaten, and only as much milk as was taken with the "cereal coffee" used. The whole day's excretion was furnished me in each case. The table following gives the important data secured as explained in the heading over each column.

| No. of sample. | Excretion in twenty-four hours. | Specific gravity at 20°. | Urine required to reduce 50 cc. of copper solution. | Ammonia from 1000 cc. of urine. | Urea from 1000 cc. of urine by Liebig process. | Uric acid from 1000 cc. of urine. | Creatinin from 1000 cc. of urine. | Chlorine from 1000 cc. of urine. | $P_2O_5$ from 1000 cc. of urine. |
|---|---|---|---|---|---|---|---|---|---|
| | cc. | | cc. | Mg. | Gms. | Mg. | Mg. | Gms. | Gms. |
| 1 | 800 | 1.029 | 16.2 | 745.0 | 28.9 | 668.5 | 1551.6 | 6.65 | 1.89 |
| 2 | 805 | 1.030 | 16.3 | 522.0 | 28.8 | 645.0 | 1288.7 | 9.66 | 1.77 |
| 3 | 850 | 1.030 | 18.1 | 431.7 | 30.6 | 693.7 | 556.0 | 8.44 | 2.07 |
| 4 | 610 | 1.031 | 18.2 | 607.3 | 28.5 | 622.5 | 87.4 | 9.15 | 2.09 |
| 5 | 975 | 1.032 | 17.3 | 944.2 | 40.7 | 930.0 | 958.8 | 6.60 | 2.41 |
| 6 | 920 | 1.031 | 18.5 | 854.1 | 34.7 | 817.5 | 1123.7 | 7.88 | 2.38 |
| 7 | 494 | 1.030 | 16.7 | 507.7 | 32.4 | 765.0 | 362.8 | 6.10 | 1.40 |
| 8 | 1040 | 1.023 | 25.7 | 483.9 | 27.5 | 626.2 | 170.7 | 6.24 | 1.81 |
| 9 | 685 | 1.032 | 16.5 | 896.8 | 36.6 | 753.7 | 795.9 | 6.17 | 2.40 |
| 10 | 1025 | 1.029 | 19.6 | 982.2 | 33.8 | 588.7 | 847.6 | 5.75 | 2.50 |
| 11 | 1065 | 1.029 | 21.1 | 640.5 | 29.2 | 746.2 | 1337.3 | .... | .... |
| 12 | 850 | 1.030 | 19.1 | 716.5 | 31.9 | 810.0 | 1157.8 | .... | .... |

[1] This Journal, **22**, 309.

| No. of sample. | Excretion in twenty-four hours. | Specific gravity at 20°. | Urine required to reduce 50 cc. of copper solution. | Ammonia from 1000 cc. of urine. | Urea from 1000 cc. of urine by Liebig process. | Uric acid from 1000 cc. of urine. | Creatinin from 1000 cc. of urine. | Chlorine from 1000 cc. of urine. | $P_2O_5$ from 1000 cc. of urine. |
|---|---|---|---|---|---|---|---|---|---|
| | cc. | | cc. | Mg. | Gm. | Mg. | Mg. | Gm. | Gm. |
| 13 | 800 | 1.031 | 17.1 | 626.3 | 34.8 | 843.7 | 790.1 | .... | .... |
| 14 | 1020 | 1.028 | 19.2 | 498.2 | 28.8 | 705.0 | 889.6 | .... | .... |
| 15 | 850 | 1.030 | 20.2 | 711.7 | 32.2 | 952.5 | 1082.7 | 9.77 | .... |
| 16 | 800 | 1.030 | 17.9 | 1043.9 | 38.8 | 731.2 | 1137.2 | .... | .... |
| 17 | 950 | 1.027 | 22.8 | 616.8 | 28.6 | 656.2 | 1017.4 | 8.17 | .... |
| 18 | 1020 | 1.027 | 22.7 | 607.3 | 26.8 | 645.0 | 1003.0 | 10.19 | .... |
| 19 | 800 | 1.031 | 16.1 | 683.2 | 33.2 | 1166.2 | 1558.8 | 7.68 | .... |
| 20 | 950 | 1.031 | 19.2 | 1062.8 | 35.8 | 843.7 | 805.7 | 9.02 | .... |
| 21 | 925 | 1.030 | 17.3 | 1262.1 | 37.1 | 978.7 | 1157.8 | 9.06 | .... |
| 22 | 905 | 1.030 | 18.4 | 1072.3 | 34.2 | 746.2 | 1547.0 | 9.38 | .... |
| 23 | 860 | 1.030 | 17.2 | 920.5 | 41.6 | 780.0 | 361.1 | .... | .... |
| 24 | 970 | 1.028 | 21.6 | 664.3 | 32.4 | 705.0 | 247.5 | 8.35 | 1.85 |
| Mean | 874 | 1.030 | 18.9 | 754.2 | 32.8 | 767.6 | 909.8 | 8.01 | 2.05 |

At first sight we notice the rather marked reducing powers of these urines which in the mean appears to be about 20 per cent. greater than in the cases described before. But at the same time it will be observed that these urines in general are highly concentrated, the average daily excretion being only 874 cc. as against 1167 cc. for the former series. If weakened then to the same dilution the total copper oxide reducing power, expressed in these terms, would be brought down even lower. In other words, for the daily excretion the reduction is not large. The probable reason for this will be evident from what follows.

Making due allowance for differences in concentration there is nothing noteworthy in the excretion of urea, uric acid, and ammonia, or for chlorine and phosphoric acid found in part of the cases, but for the excretion of creatinin we have remarkably low figures in general. The former investigation gave as the normal relation of uric acid to creatinin about 1 : 2, but here we have about 1 : 1.2. The value for the uric acid excretion is based on a volume of 1000 cc. but if calculated for the volume voided in twenty-four hours, is brought down to 671 milligrams, which is a fair average.

The correspondingly low creatinin points apparently to low metabolism, and is a fact of considerable importance. Creatinin is supposed to reach the urine in one of two ways. Many physiologists (for illustration see Schaefer's "Text-book of Physiology," p. 599) attribute it mainly or wholly to the creatin found in the lean meat consumed as food, and changed by dehydration in the liver, while on the other hand, it may be a product of body muscle metabolism. That it is not necessarily dependent on the creatin of meat has long been recognized by numerous writers since its appearance in urine during starvation has been abundantly demonstrated. The above tests fully confirm this view. The food of the persons furnishing the urines for experiment was certainly free from anything more than traces possibly of either creatin or creatinin, and had been for a period of months or years. Yet we find a creatinin excretion which is within the limits given as normal in many of our text-books. This must be traced to muscular creatin, formed in turn by metabolism of the food proteids. This view is rendered more probable by the discovery pointed out by several recent writers of the close relation of creatin and similar bodies to the derivatives of proteids formed by various hydrolytic cleavages. Although the simple relation suggested by Drechsel[1] in which the resemblance of creatin to lysatin was shown, no longer appears to hold since Hedin and others have made it evident that lysatin is probably a mixture of arginin and lysin,[2] we still have the creatin-like nature of arginin itself as a very interesting fact[3] pointing to the same general relation. The fact that the hexone bases are produced in trypsin digestion as well as by acid hydrolysis[4] has probably no bearing in the case in suggesting another possible source of the creatinin found, besides that of muscle katabolism, as the amounts which may be so formed are usually very small.

That the creatinin was relatively low in all the urines was probably due to low food consumption and metabolism. The men furnishing the urine performed little muscular work and took but little exercise. In a few cases the results were very

[1] *Ber. d. chem. Ges.*, **23**, 3096.

[2] *Ztschr. physiol. Chem.*, **21**, 297.

[3] Schulze and Winterstein: *Ztschr. physiol. Chem.*, **26**, 1.

[4] See papers by Kossel and Mathews and by Kutscher: *Ztschr. physiol. Chem.*, **25**, 190 and 195, in illustration.

low; this can not be explained by accidental error in the experimental methods, concentration of the urine with alkaline reaction, for example, but must depend on some relation not at present discernible. The tests were all carefully made in the same manner and precautions were taken to secure a final concentrated filtrate in which zinc chloride would certainly precipitate any creatinin present.

The distribution of the reducing power in these urines is also interesting. It will not be necessary to make the calculation for each case as was done in the former paper, but the average results may be taken. The table above gives 18.9 cc. of urine in the mean as the volume required to reduce 50 cc. of the standard copper solution containing 2.604 grams of cupric oxide to the liter. From this it may be calculated that 1000 cc. of the urine would reduce 6.888 grams of cupric oxide. This is a high figure because of the marked concentration of most of the urines. Making a similar calculation from the data of the last paper we find that the creatinin of 1000 cc. of the average urine would reduce 1.282 grams of cupric oxide, while the uric acid would reduce 1.091 grams. The sum of these reductions is 2.373 grams, or a trifle over one-third of the total reduction. We have remaining 4.515 grams of cupric oxide per liter as the amount corresponding to the carbohydrates or similar bodies present. In view of the character of the food consumed this is an interesting but not unexpected result. Allowing for the concentration the reduction due to carbohydrates is still large. It is evident, therefore, that a diet wholly vegetable, in which carbohydrates and fats predominate, favors the increase in the non-nitrogenous (probably carbohydrate) factors in the urine. My thanks are due to Mr. Frank Wright and Mr. Charles Erickson for the experimental work.

NORTHWESTERN UNIVERSITY, CHICAGO,
June 20, 1900.

## REVIEWS.

### AN EXPERIMENTAL STUDY OF RADIO-ACTIVE SUBSTANCES.[1]

Professor Röntgen's remarkable discovery, in 1895, of the penetrating rays called by him X-rays, but now equally well known by his own name, was followed in 1896 by Becquerel's announcement that the salts of uranium emit invisible radiations capable of discharging electrified bodies and of producing skiagraphic images on sensitive plates. He found that potassio-uranic sulphate emits rays that pass through black paper and affect photographic plates; this property is not limited to the brilliantly fluorescent uranic salts, but is shared by the non-fluorescent uranous salts. All uranium compounds examined proved to be active, whether phosphorescent or not, whether crystalline, melted or in solution; and metallic uranium exhibits the phenomena in a marked degree. The permanence of this property is amazing, substances kept in a double leaden box more than three years emitted rays having almost as much power as when first tested.

Shortly after the announcement by Becquerel, experimenters found that other substances have the power of emitting these "Becquerel rays;" M. Henry found it in phosphorescent zinc sulphide, Niewenglowski in insolated calcium sulphide, Troost in artificial hexagonal blende, and Schmidt in thorium compounds. In 1898 Mme. Sklodowska Curie, working in the laboratory of the Municipal School of Industrial Physics and Chemistry in Paris, devised a special apparatus for measuring the electrical conductivity of the air when under the influence of "radio-active bodies," and by its means studied the behavior of the minerals pitchblende, chalcolite, autunite, cleveite, monazite, orangeite, and thorite, and found them all active. Some varieties of pitchblende showed more than three times as much energy as metallic uranium itself, and this led her to the conclusion that the peculiar property was due to some unknown body contained in the mineral, and not to uranium compounds. Associating with her, her husband, Mme. and M. Curie attacked the mineral pitchblende with acids and reagents and soon obtained results that were presented by M. Becquerel to the Academy of Sciences, Paris, at a meeting held Monday, 18th July, 1898.

These savants showed that pitchblende contains a substance, apparently analogous to bismuth, which emits Becquerel rays

[1] Read at a meeting of the Chemical Society of Washington, held April 21, 1900, at Baltimore, Md.

4000 times stronger than uranium; they were unable to isolate the element having radiant power but they named it "Polonium," in honor of the native land of Mme. Curie. In December of the same year the lady received the Gegner prize of 4000 francs awarded her by the Academy of Sciences, and later in the same month M. and Mme. Curie, together with M. Bémont (director of the Municipal Laboratory), announced the discovery of a second radio-active body in pitchblende, which they called "Radium." Since that date Mme. Curie and her husband have industriously carried on investigations, publishing their results in the *Comptes rendus*; and some German physicists, not gallant enough to leave the enterprising woman a clear field, have announced some minor discoveries. From these papers we gather the following facts concerning these marvelous bodies.

As yet, comparatively little is known of the chemistry of the salts of polonium, since the radio-active substance has not been separated from its companions; on working up the mineral pitchblende the polonium is found in the precipitate thrown down by hydrogen sulphide, and insoluble in ammonium sulphide. Solutions of polonium react like those of bismuth, being precipitated by water.

The mixture of substances in which radium shows its activity has been more fully studied; the yet unknown element accompanies barium in analytical separations, its chloride is wholly soluble in water, and it responds to the usual tests for barium. The spectrum of the substance shows the bands of barium together with other lines peculiar to radium.[1] Attempts to separate radium from barium have been unsuccessful, but by fractional precipitation of the mixed chlorides with alcohol a salt has been obtained having 900 times the activity of uranium.

By operating on half a ton of the residues of uranium minerals, Mme. Curie obtained 2 kilograms of material rich in radium; with this, attempts were made to determine the atomic weight of radium, and she found the figures 140, the atomic weight of barium being 136.4.

The extraordinary physical properties of the rays emitted by these bodies have commanded the most attention; they possess luminosity, actinic and skiagraphic power, and render the air through which they pass a conductor of electricity. This latter property, the one which led to their discovery, is studied by means of an electroscope of special construction. It consists essentially of a gold-leaf (or aluminium foil) electroscope enclosed in a metallic box with glass sides and communicating with a metal disk exterior to the box. This disk lies in a horizontal plane a few centimeters above another parallel disk which serves as a support for the substances under examination.

[1] Demarcay: *Compt. rend.*, 129, 716, Nov. 6, 1899.

When the electroscope is charged by rubbing the upper disk with a piece of ebonite, the gold-leaf diverges from the perpendicular and will remain so for some time if undisturbed; on placing a layer of any radio-active body on the insulated lower disk the air between the two disks becomes a conductor and the gold-leaf at once resumes its normal position. To estimate the rapidity of the displacement of the gold-leaf, a microscope fitted with a micrometer eye-piece is attached to the apparatus at right angles to the axis, and with the aid of a watch beating seconds the time is noted which the gold-leaf takes to reach a certain point on the scale of the micrometer.

Becquerel first announced that the rays given out by uranium exhibited the phenomena of polarization, reflection, and refraction, but this was not confirmed by other observers and on repeating his experiments with radium and with polonium Becquerel got contradictory and negative results. The French chemist observed that the rays emitted by different bodies are very unequally absorbed; the rays of radium and uranium freely penetrate plates of quartz, fluorite, and mica, but those of polonium are absorbed by these minerals and scarcely penetrate paper. On the other hand rays of polonium pass through aluminum more freely than those of uranium.

The rays of divers origin are also influenced in different ways by a magnetic field; in an irregular magnetic field formed by a powerful electromagnet, the rays emitted by radium are deflected and concentrated on the poles; to show this, Becquerel devised ingenious experiments giving photographic records.[1] On examining the rays of polonium compounds (furnished by Mme. Curie) he found that polonium acted differently from radium,[2] and his results failed to confirm the observations of Geisel previously announced. Later, Mme. Curie also published a note on the dissimilar behavior of the rays of polonium and of radium in a magnetic field.[3] The subject has also been studied at Vienna by Stefan Meyer and Egon R. von Schweidler.[4]

Becquerel rays excite phosphorescence in gems, minerals, barium sulphide, calcium sulphide, etc.; in fluorite the phosphorescence remains twenty-four hours after the influence of radium has been removed, much as when exposed to the light of the electric arc.

In studying the power that these rays have of communicating energy to inactive bodies, Mme. Curie worked with substances so well purified that they were 50,000 times more powerful than uranium, and the induced activity measured 1 to 50 times that

1 *Compt. rend.*, 130, 996, Dec. 11, 1899.
2 *Ibid.*, Dec. 26, 1899.
3 *Ibid.*, 130, 73, Jan. 8, 1900.
4 *Phys. Zischr.*, 10, 113.

of uranium; the substances examined were zinc, aluminum, brass-foil, lead, platinum, bismuth, nickel, paper, barium carbonate, and bismuth sulphide. Her experiments showed that a true induction of radiant energy is effected, and the energy imparted to metallic plates is not removed by washing with water although the radium chloride ("chlorure de barium radifère") is soluble. The activity induced by Becquerel rays persists, while that caused by Röntgen rays ceases suddenly on removal of the agent.[1]

The actinic power of the rays is shown by exposing the salts to sensitive plates; with the relatively pure material obtained by Mme. Curie an exposure of one-half minute sufficed to get an impression. The peculiar power of Röntgen rays is seen by using a barium platinocyanide fluoroscope, the rays exciting fluorescence through aluminum, vulcanite, etc.[2]

Mme. Curie records obtaining good "photo-impressions" with uranium, uranous oxide, pitchblende, chalcolite, etc., through glass, air, and aluminum.

The spontaneous luminosity of radium compounds was announced by Mme. Curie to the Physical Society of Paris in March, 1899,[3] and in November of that year she published her discovery that the wonderful rays exert chemical action. They transform oxygen into ozone; this was first noticed by the odor of the air in a flask in which radium compounds were confined, and was confirmed by the usual test with potassium iodide starch-paper. The rays also produce a certain coloration in glass changing it to violet; and they transform barium platinocyanide from yellow to brown, in which state it is less fluorescent, but this can be revived by insolation.[4]

At the suggestion of Mme. and M. Curie, M. A. Debierne, working in the laboratory of the Sorbonne, examined pitchblende for other radio-active bodies, especially the portion precipitated from solution by ammonia and ammonium sulphide, after separation of the uranium; in October, 1899, he found associated with titanium, a substance exhibiting 100,000 times more radiant power than uranium, and having chemical properties distinct from radium and polonium. The rays emitted by this body, named actinium, have the same manifold action as the other substances, with the exception that it is not self-luminous.[5]

In a more recent paper[6] M. Debierne finds that actinium is

[1] *Compt. rend.*, **124**, 714, Nov. 6, 1899.
[2] *Ibid.*, **126**, 1101 (1898); **127**, 1215, Dec. 26, 1898.
[3] *Rev. chim. pure et appliquée*, July, 1899.
[4] *Compt. rend.*, **129**, 823 (Nov. 30, 1899).
[5] *Ibid.*, **129**, 593.
[6] *Ibid.*, **130** (April 12, 1900).

allied to thorium, and suggests that the radio-activity of the latter is due to admixture of the new substance.

To complete this review of the radio-active bodies, brief notice must be made of two papers by German chemists. Fritz Geisel obtained radium from uranium ores other than pitch-blende, and remarks: "Freshly crystallized Ba salts containing Ra are only slightly active, but in a few days or weeks they reach a maximum. They are strongest when anhydrous, moisture stops activity and heating restores it."[1]

Becquerel rays have the same intensity in partial vacuum as at ordinary air-pressure; this was proved by electrical and photographic experiments made by J. Elster and H. Geitel.[2]

Through the enterprise and liberality of the Smithsonian Institution, and by the courtesy of Secretary Langley, I have enjoyed the opportunity of studying small specimens of these rare and costly substances; they comprise 10 grams of "radio-active substances" in two portions, prepared by E. de Haen, manufacturing chemist of Hannover, Germany, and 4 grams of "chlorure de barium radifère," and 4 grams of "polonium subnitrate" from the "Société Centrale de Produits Chimiques (Ancienne Maison Rousseau)", Paris, said to be prepared according to the instructions of Mme. and M. Curie.

The samples from Hannover were marked "A" and "B" respectively, and a memorandum accompanying them stated that "B" excites fluorescence in barium platinocyanide more energetically than "A," whereas the latter is self-luminous; as a matter of fact I found both luminous in the dark and "B" the brighter of the two.

The specimens were enclosed in hermetically sealed bottles and protected from light by straw-board cylinders; on removing the wrappings in a dark room both were seen to emit greenish white light that gave to the enveloping papers a peculiar glow, similar to the fluorescence produced by Röntgen rays. I here call especial attention to the fact that during all the time that I have had the substances under examination they have been kept in the dark, no light reaching them stronger than that of the yellow and orange-red of a photographic dark room, so that insolation has played no part in renewing their energy.

The grayish white powders proved to be wholly soluble in water and the solution gave the usual reactions for barium chloride.

Moistening the radium chloride with cold water does not immediately stop emission of light, but on heating to boiling, the luminosity ceases. The water was expelled and the material, heated in a platinum dish to dull redness, resumed its luminosity

[1] *Ann. Phys. Chem.*, 69, 91 (1898).

[2] Wied. *Ann.*, 66, 135 (1898).

after a few days *in the dark*. The fact that radium compounds resume their power of emitting light slowly has been noted by Geisel, but he fails to state whether the salt regains its property without exposure to sunlight.

The substances "A" and "B" were examined with a fluoroscope at first without success, but in a perfectly dark room, after the eyes became sensitive, the screen of barium platinocyanide was distinctly seen to fluoresce feebly.

The small specimens of these bodies had no perceptible influence in exciting phosphorescence of sulphides of the alkaline earths exposed to their action.

Having at hand no apparatus for measuring the electrical conductivity of the air, my experiments were chiefly directed to ascertaining the action of the rays on sensitive plates.

The photographic experiments were made with Seed non-halation dry plates (No. 26). To test the approximate actinic power of the bodies "A" and "B," sections of sensitive plates at distances of 5 and 10 inches were exposed at intervals of from two to twelve minutes; these gave bands varying in intensity with the duration of action. "B" showed far greater power than "A". By exposing sensitive plates behind an ordinary negative to the entire 10 grams of "radium" from two to three hours, good transparencies were obtained; on substituting Eastman's bromide paper, prints were secured; the distance of the sensitive surfaces from the source of light was about 3 inches.

To get skiagraphic images, plates were enveloped in Carbutt's black paper (non-permeable to light) and on this was laid a piece of tin-foil cut in open work pattern; after one hour's exposure a negative was obtained plainly showing the pattern. "A" was apparently stronger than "B".

Analogous experiments were carried out with the specimens of "radium" and of "polonium" from Paris; making allowance for the difference in weight, the radium of German origin was about five times as active as the French. The sample labeled "polonium subnitrate" (weighing 4 grams), had positively no action on the plates used.

Having at my disposal 500 grams exceedingly well purified uranic nitrate (remaining from previous researches), I examined it for Becquerel rays, but a sensitive plate exposed three hours to the beautifully fluorescent crystallized salt gave no trace of action. Similar negative results have been obtained by Sir William Crookes.

The primary source of the energy manifested by these extraordinary substances has greatly puzzled physicists and as yet remains a mystery. Mme. Curie speculating on the matter, at first proposed the following explanation: she conjectured that all space is continually traversed by rays analogous to Röntgen

rays but far more penetrative, and not capable of being absorbed by certain elements of high atomic weight such as uranium and thorium.

Becquerel, reflecting on the marvelous spontaneous emission of light, remarked: if it can be proved that the luminosity causes no loss of energy, the state of the uranium is like that of a magnet which has been produced by an expenditure of energy and retains it indefinitely, maintaining around it a field in which transformation of energy can be effected. But the photographic reductions and the excitation of phosphorescence in a sensitive screen require an expenditure of energy, of which the source can only be in the radio-active substances. As this expenditure is slight perhaps the bodies have a large reserve of energy which can be drawn upon for years without showing loss; at any rate it has been impossible, says Becquerel, to bring about any appreciable variation in the intensity of the emission by physical influences.

Somewhat later Becquerel hazarded the opinion that the radiation of radium is composed at least in part of cathodic rays; but these have been proved to be material, hence the induced activity must be caused by material particles impinging upon the substances excited. This materialistic theory seems to be confirmed by the results of ingenious experiments made by Mme. and M. Curie; they placed a sensitive plate beneath a salt of radium supported upon a slab of lead, in the vicinity of an electromagnet. Under these conditions when the current was passing, the rays emitted by the chemical salt were bent in curved lines upon the sensitive plate, making impressions.

It may be objected, says a French writer in the *Revue générale des Sciences* that this theory requires us to admit actual loss of particles of matter, nevertheless the charges are so feeble that the most intense radiation yet observed would require millions of years for the removal of 1 milligram of substance.

The same writer raises the question, which of the observed phenomena is the primary one? does the radiation of radium excite cathodic rays, or do the latter exist in the chemical compounds? and he regards the latter as improbable. The primordial source of energy in radium probably resides, he adds, in the ultraviolet light, and the efflux of material particles that ensues is only a secondary phenomenon, but on a far larger scale than has previously been observed.

Speculations as to the future history and applications of these wonder-working bodies press upon even the dullest imagination; if a few grams of earth-born material, containing probably only a small percentage of the active body, emit light enough to affect the human eye and a photographic plate, as well as rays

that penetrate with X-ray power, what degree of luminosity, of actinism, and of Röntgenism, is to be expected from an hundredweight of the quintessence of energy purified from interfering matter?

And to what uses is this light-generating material to be applied? Are our bicycles to be lighted with disks of radium in tiny lanterns? Are these substances to become the cheapest form of light for certain purposes? Are we about to realize the chimerical dream of the alchemists,—lamps giving light perpetually without consumption of oil?

Seriously, in what direction is profound study of these substances going to lead us? Will it not greatly extend our knowledge of physical manifestations of energy and their correlation? What bearing will this power of "opening up paths through the air" for currents of electricity have upon our knowledge of heat, light, electricity, and those forms of energy called by the names of Röntgen and Becquerel?

In what corner of the globe will be found the cheap and convenient supply of raw material yielding the radio-active bodies? Will not chemists be obliged to reexamine much known material by laboratory methods conducted in the dark? Many of us have worked up kilograms of pitchblende to extract uranium oxides and in so doing have poured down the waste-pipe or thrown into the dust-bin the more interesting and precious radio-active bodies.

At all events whatever the future may bring, physicists are deeply indebted to Becquerel, and to Mme. and M. Curie for placing in our hands new methods of research and for furnishing a novel basis for speculations destined to yield abundant fruits.

## POSTSCRIPT.

Bela von Lengyel, of Budapest, has pointed out that the chemical evidence is insufficient to establish the elementary character of these radio-active bodies, and claims to have prepared the so-called "radium" synthetically. By fusing with the heat of the electric arc uranic nitrate mixed with 2 to 3 per cent. of barium nitrate, and treating the mass with nitric acid, water, and sulphuric acid, successively, he obtained radio-active barium sulphate possessing all the physical properties characteristic of the "element" announced by Mme. Curie. The resulting substance gives out actinic rays, Röntgen rays, excites platinocyanide screens, and causes air to conduct electricity.

The Hungarian chemist has made and examined the chloride and the carbonate of this substance and finds that they have the same properties; he wishes his paper regarded as a preliminary notice, proposing to continue his researches.

Von Lengyel's paper was received by the German Chemical Society on April 2nd, but the number of the *Berichte*[1] containing it only reached Washington on May 26.

Admitting that radio-active bodies can be manufactured to order, are we any nearer explaining their mysterious powers?

HENRY CARRINGTON BOLTON.

COSMOS CLUB, WASHINGTON, D. C., May 26, 1900.

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## MODERN RESEARCHES ON THE CHEMISTRY OF THE PROTEID MOLECULE.[2]

It is impossible, at the present stage of our knowledge, to give any satisfactory definition of a proteid, based either on its physiological or chemical properties. Physiologically, it can be pointed out as the main constituent of all cells and tissues. In regard to its chemical properties, it can be stated with absolute certainty that it consists of carbon, hydrogen, oxygen, nitrogen, and sulphur. It does not possess very marked acid or basic properties, but forms salts with both bases and acids, its affinity for both being very weak.

I.

It can not be classified under any of the well-established groups of chemical compounds. Some attempts in this direction, however, have been made in recent years; and of these, the attempt to classify all proteids among glucosides has been the cause of much dispute from the experimental and speculative side of the question. The author of this theory and its most enthusiastic advocate was Pavy, who, by hydrolysis of egg albumin, succeeded in obtaining a reducing substance, capable of combining with phenylhydrazine, forming an osozone of a definite melting-point.

Physiologists, who were all inclined to see the source of the tissue-carbohydrates in the tissue-proteids, naturally welcomed Pavy's work, and were ready to endorse his views. A number of researches, however, were undertaken in order to test the correctness of Pavy's statements. The results thereof were contradictory. Morner has investigated, in that direction, serum globulin, and found that on heating with 3–5 per cent. hydrochloric acid, it yielded a solution capable of reducing Fehling's solution. Krawkow has tested, in the same direction, various proteids with different results. Substances combining with phenylhydrazine, giving osozone, were obtained by him from

[1] Vol. 33, p. 1237, May 14, 1900.

[2] Read before the New York Section of the American Chemical Society, May 11, 1900.

egg albumin (m. p. 183°–185° C.), fibrin (m. p. 182°–184° C.), and serum albumin (m. p. 183°–185° C.). He failed to obtain similar substances, or obtained them only in traces from serum globulin, lactalbumin, casein, gelatin, vitellin, and mucoid.

The work which followed that of Krawkow was done by Eichholtz and is instructive in many ways. Thus, in contradiction to Krawkow, he failed to obtain the carbohydrate from serum albumin and succeeded in obtaining it from serum globulin. Of greater interest, however, is the fact that he found in the white of the egg, besides the ovomucoid, a substance related to it, which he called "ovomucin."

In regard to the egg albumin, two other researches are of great importance: first, that of Weydemann, who obtained on treatment of egg albumin with a 10 per cent. solution of sodium hydroxide, a substance similar to "animal gum"; and secondly, the work of Spenzer, who repeated, under Drechsel's direction, the experiments of Pavy. Spenzer was very careful to remove all the mucoid from the white of the egg, and only used such methods as would exclude the contamination of the egg albumin with the carbohydrates of the filter-paper, etc. Under such conditions, Spenzer failed to obtain a carbohydrate on the hydrolysis of egg albumin with acids.

A comparison of the results of all the authors reveals the fact that proteids of the same nature gave different results to different investigators, as can be seen from the following table:

| | Pavy. | Krawkow. | Eichholtz. | Morner. | Spenzer. |
|---|---|---|---|---|---|
| Egg albumin ..... | positive | positive | positive | ..... | negative |
| Fibrin..... | " | " | ..... | ..... | ..... |
| Serum albumin ... | " | " | negative | ..... | ..... |
| Serum globulin ... | " | negative | positive | positive | ..... |
| Lactalbumin ..... | ..... | " | ..... | ..... | ..... |
| Casein ..... | positive | " | ..... | ..... | ..... |
| Gelatine ..... | negative | " | ..... | ..... | ..... |
| Vitellin..... | positive | " | ..... | ..... | ..... |
| Mucoid ..... | ..... | " | ..... | ..... | ..... |

Further, new substances related to mucins were discovered where they were not suspected by some of the investigators searching for carbohydrate in the proteid molecule; and finally, those who were more careful in avoiding contamination were the least successful in obtaining the "carbohydrate moiety" of the proteid molecule. It seems therefore unwarranted at the present moment to accept the existence of such a moiety.

## II. THE NITROGEN.

The greatest part of the researches on the chemistry of proteids has been directed to the character and form of the nitrogen present in its molecule. The older authors knew that the nitro-

gen was not all in equally strong combination with the rest of the proteid molecule, and that the nitrogen entered the proteid molecule in the form of an amido group. But of the amido compounds only those of the monamido acids were detected in that molecule. A great part of the nitrogen was in a combination unknown to most of the old investigators. Drechsel was the first to investigate with great success the nature of the nitrogenous residue. He has found that it consists of substances with a well-defined basic nature, some of them being diamido acids. The substances he discovered were lysin and lysatine: one being diamidovalerianic acid, $C_6H_{14}N_2O_2$; the other a homologue of creatine, $C_6H_{13}N_3O_2$. Later he also discovered among the decomposition products of proteids diamidoacetic acid. A number of different proteids were examined by the students of Drechsel, namely, E. Fisher, Siegfried, and Hedin, and the presence of the bases lysin and lysatine was demonstrated in all of them. Furthermore, Siegfried isolated besides these two bases, a new one having the composition $C_{11}H_{20}N_6O_6$. Hedin then obtained, by the decomposition of different proteids, arginin, a base of the following formula:

$$HN=\overset{NH_2}{\overset{|}{C}}-NH.CH_2.CH_2.CH_2-\overset{NH_2}{\overset{|}{CH}}-COOH,$$

and which was first described by E. Schulze as a constituent of vegetating seeds. Later Hedin also demonstrated that the substance, described by Siegfried as $C_{11}H_{20}N_6O_6$, was histidin—$C_6H_9N_3O_2$—a base first discovered by Kossel as a decomposition product of a protamine, "sturin."

The statement of R. Cohn that a pyridin base could be detected among the other basic decomposition products of the proteids was very recently retracted by him.

After the presence of the basic substances in the proteid molecule was demonstrated, the question arose, how are they grouped in the molecule? and the researches of Kossel seemed to fully answer it. Kossel has resumed the work of Miescher on protamines—substances occurring mostly in fish sperm in combination with nucleic acid. The protamines had some properties common with proteids; namely, they gave the same color reaction with an alkaline copper solution as the proteids, a test known as the "Biuret test," undergoing also the same changes in solubility as proteids on digestion with pepsin hydrochloric acid.

Finally they yielded on decomposition the basic substances met with on decomposition of other proteids. The points of difference were that the protamines did not give the other color tests peculiar to proteid material and did not contain the other decom-

position products met with on decomposition of proteids except the "hexon" bases. The conclusion was natural that the property of the proteids to give the biuret test was due to the presence in its molecule of a protamine group. Such actually was the conclusion of Kossel, and, according to his theory, the protamine is the nucleus of all proteids in the same manner as benzene is the nucleus of all the aromatic compounds.

On further investigation, however, it was found that only one protamine, namely sturin, yielded, on hydrolysis with acids, all the three "hexon" bases, sturin yielding as well amidovalerianic acid. The other protamines, such as clupein, scombrin, salamin, yielded only arginin, amidovalerianic acid, and an unknown residue. Cycloytelin contained besides these an aromatic group. Thus it appeared that the biuret color test is not peculiar to one certain "protamine group," and from this standpoint there is no reason to believe that all the proteids are derivatives of one protamine.

The analysis of animal proteids by Larrow and of plant proteids by Schulze, Mendel, and Levene, which have been made up to the present time, have revealed in all of them the presence of the three hexon bases. This would seem to corroborate the view that in proteids the biuret reaction is due to a "protamine." An objection to the latter assumption, however, can be found in the researches of H. Schiff.

H. Schiff has demonstrated that the biuret reaction can be obtained from different substances which contain two $CONH_2$ groups combined together, either directly, like oxamide $\begin{matrix} CONH_2 \\ | \\ CONH_2 \end{matrix}$ or joined on a single carbon or nitrogen, like biuret $NH\begin{matrix} CONH_2 \\ \diagdown \\ \diagup \\ CONH_2 \end{matrix}$ or malonamine, $CH_2\begin{matrix} CONH_2 \\ \diagdown \\ \diagup \\ CONH_2 \end{matrix}$. Another requisite is that the $CONH_2$ groups be combined in an open chain.

Thus H. Schiff has established the fact that the property giving the biuret color test is peculiar to more than one substance, that this property is due to the presence in the molecule, not of amido groups or amido acids, but of two of the radical $CONH_2$ grouped in a certain way; that it is not very probable that a combination of "hexon" bases (which, according to Kossel's first surmise, constituted the protamine molecule) will necessarily give the biuret test; that, finally, in the protamines as well as in other proteids the peculiar color formed on addition of alkaline copper solution is due to the presence in their

respective molecules of a substance common to all of them, possibly, but perhaps not yet discovered. Attempts were also made to estimate the quantities of the different nitrogenous compounds in the molecules of different proteids, so as to establish a basis for their chemical classification. Hansemann has analyzed with this in view a great number of proteids, finding that the proportion of these constituents varied greatly with the character of the proteid. Henderson has, however, demonstrated that the temperature and the duration of the decomposition has a great influence on the formation of the different nitrogenous constituents, and thereby the conclusions of Hansemann lose much of their weight.

### III. SULPHUR.

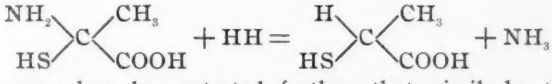
It has been accepted that the proteid molecule contains more than one atom of sulphur, and that the different atoms are in different forms of combination. This view is based on the fact that proteids heated with a solution of sodium hydroxide generally gave up part of their sulphur in the form of hydrogen sulphide, and the rest of the sulphur was detected only by means of strong oxidation, like fusion with sodium hydroxide and nitrate. Attempts have been made to establish the ratio between the different atoms. However, the methods employed by the older authors were not faultless, as the possibility of an oxidation of a part of the hydrogen sulphide into sulphuric acid (on heating with sodium hydroxide) was not excluded. The question thus needed new consideration, and such was given to it by F. N. Schultz. Great care was taken by the latter to prevent the possibility of oxidation of hydrogen sulphide, and in most experiments only about one-third of the total sulphur could be obtained in the form of hydrogen sulphide.

Very little has been known in regard to the nature of that part of the sulphur which could not be obtained as hydrogen sulphide. The opinion that it is in an oxidized state has been proved to be erroneous.

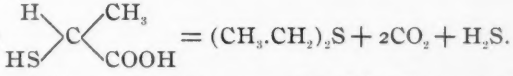
In recent years a few researches have appeared which throw some light on the subject, although none of them gives a final solution to the problem. Drechsel found among the basic decomposition products of the proteids, a substance which, on treatment with alkalies, yielded ethyl sulphide. He, therefore, concluded that the substance must be a sulphin base or a thetin compound; and that a quadrivalent sulphur was present in the proteid molecule.

A short time after Drechsel's discovery, Suter working in Baumann's laboratory, isolated from the decomposition products of proteids thiolactic acid, and very recently Morner has suc-

ceeded in obtaining, under the same conditions, cystein, which is a derivative of the former, as can be easily seen from the formulas.



Baumann has demonstrated further that similarly to the thetin compounds, the cystein or thiolactic acid yields ethyl sulphide on treatment with alkalies, according to the following formula:



Thus, another explanation was offered for the appearance of ethyl sulphide among the decomposition products of proteids. It must be remembered that both the substances ethyl sulphide and cystein (cystin) had been detected in animal secretions long before they could be obtained directly from proteids. The former was first identified in the urine of a dog by J. Abel; the latter by Baumann.

### HALOGEN PROTEIDS.

Considerable study has been devoted to the halogen derivatives of the proteids; it was expected that the latter compounds would be of great aid in explanation of the constitution of the proteid molecule. The expectations, however, have not been realized up to the present date; although the future may be more successful.

### SYNTHESIS.

Notwithstanding that little regarding the chemical constitution of the proteid molecule is established, attempts have already been made to obtain a proteid synthetically. In recent years the attempt was made by Lilienfeld, who stated in 1894 that he was successful in obtaining a synthetical proteid in the following way:

Curtius and Goebel found that if glycocoll-ethyl ester was allowed to stand, it yielded glycocoll and a biuret-giving substance which Lilienfeld claimed could form a condensation product with the ethyl ester of leucin, tyrosin, or aspartic acid, which product resembled peptone very closely.

More recently, Lilienfeld has modified his method and obtained proteids on condensation of phenol with glycocoll or with asparagin, etc.

Klimmer, however, justly remarks that Lilienfeld's substance could scarcely be considered a peptone on the following grounds:

1. The substance obtained by Lilienfeld yields readily, on decomposition, phenol and glycocol which other proteids do not, and the color which the substance takes, on treatment with alkaline copper solution, is not a color resembling the biuret reaction very closely.

Thus, little progress has been made towards the elucidation of the chemistry of the proteid molecule and its various parts. Attempts have been made to determine the weight of the molecule as a whole. According to Sabanejeff and Alexandrow, it is 14,900.

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P. A. LEVENE.

# THE PRESENT CONDITION OF THE COAL-TAR INDUSTRY.[1]

As the end of the century approaches it is interesting and instructive to look back and note the wonderful growth of the chemical industries and the great changes they have undergone, especially in the last few years, in which many of them have been revolutionized.

It may be of interest to some to consider the growth and present condition of one of the greatest of these, that of coal tar and its products.

This industry which originated in the endeavor to utilize a troublesome by-product, has grown to be the one which without doubt employs more scientific men in its study and development than any other, and a description of all its products and their manufacture would be a review of the greater part of the organic chemistry of to-day.

About 1822 coal tar was first distilled in England, but it was not until 1856, the date of the discovery of the first aniline colors, that the industry became an important one; and it is in the last twenty years only that it has attained its present gigantic proportions.

At first the entire supply of tar was derived from the distillation of coal in the manufacture of illuminating gas, but under the constantly increasing demand, new sources have been developed, and these latter may in time become our main supply.

The coal tar produced in modern gas plants is quite different from that of some years ago. Cast-iron retorts were then used and the temperature of carbonization was comparatively low. The tar in consequence was generally quite fluid and contained considerable toluene, xylene, and phenols, some naphthalene and free carbon. With the introduction of fire-clay retorts, a marked change was noted and to-day the extreme high heat produced by the use of regenerators yields a tar which, considered from the standpoint of the distiller, is of much poorer quality.

The aim of the gas manufacturer is to get the largest amount of gas of good quality that can be obtained from the kind of coal carbonized. The high temperatures employed to do this cause the volatile products as they are evolved during the distillation to be decomposed in contact with the intensely heated sides of the retort with separation of free carbon, and, as exhausters are universally used, this is drawn out with the gases and deposited with the tar.

[1] Chairman's address at the annual meeting of the Philadelphia Section, May 17, 1900.

The higher phenols and hydrocarbons are split up with formation of large quanties of naphthalene; therefore, the tar is heavier in gravity and thicker in consistency on account of the presence of more naphthalene and carbon and less of the liquid portions.

As the use of coal-tar products became more general, the demand for tar increased and in consequence the price advanced. The supply being to a certain extent fixed, manufacturers were stimulated to look for other sources of supply. Several plants were built in Europe and one in America having the production of tar and ammonia as their chief aim, but these were soon found to be unprofitable. Attention, however, had been called at an early date to the waste of these by-products in the manufacture of coke, and inventors without number entered the field with ovens designed to produce a good coke and at the same time save the tar and ammonia. A number of these, varying in minor details of construction, have been found to work well in practice,—besides, many beehive ovens have been provided with condensing plants for collecting the by-products. The tar obtained from these latter ovens and also from the gases of blast-furnaces is, however, quite different in composition from that obtained from gas works or improved coke ovens.

The temperature at which the coal is carbonized in the former being much lower, the tar contains practically no aromatic bodies, and when distilled yields oils which are free from naphthalene, benzene, and phenol, but instead contain compounds of the paraffin series, large amounts of higher complex phenols and paraffin; such tars are, therefore, of no value to the manufacturer of refined coal-tar products.

In the United States, owing to the extended use of oil and carburetted water-gas, the output of coal tar has been very much less in proportion to the population than in Europe, and it has been heretofore necessary to make up the deficiency by importing creosote oil and pitch. In the last few years, however, there has been a considerable addition to the domestic supply. A number of beehive ovens have been fitted with condensing plants and large batteries of improved coke ovens have been erected, and from these a fine grade of coke and considerable tar is obtained. The American coals appear to be much richer than those carbonized abroad.

In these ovens none of the charge is burnt to supply the heat necessary for the carbonization, as is the case with the older forms of ovens, and therefore, the yield of coke is very much larger, and may even amount to more than the analysis of the coal would seem to warrant, this being due to the deposition of carbon on the surface of the coke by the decomposition of a part of the tar as it is distilled.

The fact of a larger yield and purer quality of coke must, it seems, finally force other manufacturers to adopt improved ovens, and if even a part of the 20,000,000 tons of coke yearly produced in this country was made in such ovens with recovery of tar, we would pass from the condition of a shortage of supply to a veritable flood of tar, for even a small portion of which there would not appear to be a market.

One of the forms of ovens successfully introduced is the Semet-Solvay, of which about 300 are in operation in this country. Those interested in the subject will find a full description of them in an article by J. D. Pennock, which appeared in this Journal[1] in 1899.

The Otto-Hofmann ovens are used very extensively abroad, and through the kindness of Dr. Schniewind, chemist of the company, I am informed that 680 ovens are in operation in the United States, and that 400 are now being erected in Canada. The most interesting of these plants is that at Everett, near Boston, Mass., where 400 ovens are in successful operation. These have been fully described and illustrated by Dr. Schniewind in articles which have appeared in the *Progressive Age*. The plant is so situated that coal from Nova Scotia can be discharged directly from the steamers, and labor is reduced to a minimum by the use of every modern appliance for handling the materials used and produced.

The gas as it distils being higher in candle-power in the first hours of carbonization, this portion is collected by itself and after removal of tar and ammonia, is supplied to the city of Boston and vicinity. The gas coming off in the latter part of the distillation is used, after the tar has been removed, to heat the ovens. The coke is equal in quality to the best metallurgical coke and is sold for this purpose or broken into various sizes for domestic use.

It would seem that this novel and interesting application of the coke oven is destined to come into general use for large cities.

The tar from these ovens resembles the average retort tar except that it does not contain as much low-boiling hydrocarbons or phenol.

A certain amount of tar is also obtained from the manufacture of oil- and water-gas but they are of much less value than pure coal tar. The water-gas tar is especially difficult to utilize as it contains from 50 to 75 per cent. of water in the state of an emulsion which will not separate on standing.

In the United States tar is usually distilled into light oil, heavy oil, and pitch. The light oil comprises the first portions of the distillate until the oil, as it runs off, sinks in water. The

[1] This Journal, 21, 678.

entire distillate when mixed has a gravity from 0.93 to 0.98. Its nature has varied with the change in the tar as noted above, formerly they were quite fluid, but now in most cases they are semisolid from naphthalene.

The pitch remaining in the still after the distillation is known as soft pitch, and is adapted for roofing or paving purposes.

Formerly it was customary to run to hard pitch which was sent abroad to be used in the manufacture of compressed fuel; the anthracene oil obtained by this distillation was filtered and the anthracene pressed in hydraulic presses, making 40 per cent. anthracene. This was shipped to England and used in the manufacture of alizarin. At that time anthracene was one of the most valuable of the crude tar products, but the price has now fallen so low that it does not pay to export it, and there is very little sale for hard pitch as the manufacture of briquettes for fuel is carried on in a limited way only. The manufacture of anthracene has, therefore, been abandoned for some years.

The demand for creosote oil has, on the contrary, been constantly increasing owing to its extensive use in creosoting lumber, a number of plants for this purpose being in operation here.

Oil for this purpose is required to conform to certain specifications; formerly it was deemed necessary to have a large amount of tar acids, but now it is recognized that the naphthalene is a much more important agent in the preservation of lumber; and in consequence, specifications require 40 to 50 per cent. to be present, and in cold weather the oils are often entirely solid from separated naphthalene. In this connection, it is well to call attention to the fact that many specifications call for 50 per cent. of naphthalene and yet require the oil to be limpid at 90° F., which is an impossibility when such a large amount of naphthalene is present.

When we come to consider the refined products of coal-tar we can, in the short time at our disposal, mention only the most important. In general it may be said that each year greater purity is demanded by consumers, and a large number of the commercial products are practically chemically pure.

This branch of the industry has not made as great strides in the United States as it should. A severe blow was dealt when nearly all the protective duties were removed a few years ago. Formerly there was on the most of them a duty of 20 per cent. which enabled the American manufacturer to compete notwithstanding the higher wages ruling here.

The use of special labor-saving machinery which has done so much to enable our manufacturers to enter the markets of the world is not an important factor in this industry, which, owing to its nature, does not permit the extensive use of such labor-

saving devices, and where machinery can be used, we find the German manufacturers, who are our chief competitors, have the most improved devices in this line.

If we compare the estimates of cost of manufacture by American and German experts, the item of labor is seen to be a very serious one. For ordinary labor we must pay from 14 to 15 cents per hour, German estimates are based on 6 to 7 cents. In the pay of skilled mechanics the difference is even more striking: carpenters, masons, machinists, boiler and tank makers, receive from 30 to 45 cents per hour, while the prices abroad are scarcely 50 per cent. of these. This has a twofold effect on the industry: first, in increasing the item of repairs and maintenance, which, owing to the nature of the business, is a very large one, necessitating the constant renewal of parts destroyed in the processes. Second, it handicaps the manufacturer by requiring a larger outlay of capital to erect the plant than is the case abroad. A conservative estimate would be that an average plant would cost twice as much here as in Germany.

Of all the refined products, benzene has probably been subject to the greatest fluctuations. The demand for this article increased so rapidly that the price became very high, and efforts were made in all directions to perfect processes which would produce it independently of the gas works. It was at this time that the endeavor was made both in Europe and America to distil coal in retorts at the mines with the making of benzene as their prime object; but, as already stated, these were soon abandoned. A plant was also built in Ohio to manufacture benzene and its homologues from petroleum residues but without success.

Attention had been called at an early day to the large amount of benzene present in the coal gas, amounting to about twenty times as much as is present in the tar from the same gas. It was manifestly impossible to remove it from the gas without destroying, to a large extent, its illuminating power, but this objection did not hold good with the gas obtained from the improved coke ovens, and appliances were added to these plants to remove this benzene. A large number of such plants are in operation abroad at this time; the gas from the ovens after removal of tar and ammonia is forced through specially designed towers, in which the gas is brought into intimate contact with a fraction of oil from coal tar. This oil absorbs the benzene, and when saturated, is heated, and the crude benzene driven out. The product thus obtained is equal to about 90 per cent. benzene; that is to say, consists of about 70 per cent. benzene, 20 to 25 per cent. of toluene, and the balance of higher bodies. The introduction of these benzene extracting plants may be said to have been *too* successful, as the price has fallen to such an

extent that the extraction at present is hardly remunerative. We are, however, assured of a source of supply which can be readily increased as the demand warrants. The present supply is undoubtedly more than the demand; toluene, however, is not obtained in such large quantities by this method and as the demand is steadily increasing owing to many new uses, among them the manufacture of artificial indigo, the price has advanced so that it is now selling abroad at a higher price than benzene, while formerly the reverse was the case. At the present time there is no plant in operation in this country extracting the benzene from gas.

The low price of benzene permits it to be used in many industries as a solvent for the extraction of chemicals and drugs, and immense quantities are used abroad for enriching gas.

Naphthalene is one of the coal-tar products which is now manufactured on a very large scale in a great degree of purity. This article has advanced considerably in price owing both to the great demand, and to the fact that crude naphthalene is now readily sold without removal from the creosote oil for reasons stated above. Before the duties were removed, there were three factories manufacturing the article in this country; since it has been placed on the free list only one of these survives. The output is chiefly used as a substitute for camphor for destroying moths.

Crystal carbolic acid or phenol is one of the few tar products which has not suffered the general decline.

In all the varied new sources of supply of other tar products, none has been found which promises increased output of phenol. The coke oven tar does not appear to yield much phenol, so that while the supply is constant or perhaps increasing slightly, it does not keep pace with the large demand, the chief of which is for the manufacture of picric and salicylic acids. A limited amount of phenol is made in this country, and considerable refined from imported materials, but the great bulk comes to us in a finished condition from Europe.

Nitrobenzene, nitrotoluene, and other nitro compounds are made in one factory, the output being mainly used by manufacturers of colors and explosives. A certain quantity of rectified nitrobenzene, known as oil of myrbane, is used by manufacturers of soaps and oils.

Aniline oil which is made in such large quantities abroad is not made at present in this country. Its manufacture was undertaken a number of years ago by makers of colors but abandoned as it was found the article could be imported at less cost. A factory, however, is now being equipped for its manufacture, and in a few weeks will be in operation.

Acetanilide is made by two or three factories and they supply nearly all the requirements of this market.

When the tariff on coal-tar products was revised and most articles placed on the free list, for some reason, salicylic and benzoic acids were singled out from all other compounds and favored with the specific duty of 10 cents per pound. In consequence, a number of works are now producing the former acid, using imported phenol.

The finer organic compounds are apparently not produced except vanillin, which is being made by at least two if not three firms.

Notwithstanding the great competition of Europe in aniline colors, the American manufacturers have in the last few years made decided strides, although as yet they appear to have confined themselves to the older standard colors. They are aided by a duty of 20 per cent. with practically all their raw materials free. They still labor, however, under the disadvantage of having to import a great deal of their supplies. There are at present five factories in operation.

It will be seen from this rapid review that there is still a wide field for the chemist and manufacturer in this country; and with a gradual increase in the output of crude materials, it is to be hoped and expected that in a few years we will produce a large amount of the enormous quantity of these products now imported.

England appears to have fallen out of the race in the competition for the American trade, especially in the finer coal-tar products, and Germany is now in the lead, even competing with England in the cruder preparations. To show the important position held by Germany, attention is called to the statistics compiled by the German government up to July 1898, on which date there were 25 factories devoted to anilin and anilin dyes, and 48 establishments which made dyestuffs, carbolic acid, and other coal-tar preparations. Among the exports for 1898 were:

9,321 metric tons, alizarin,
19,712 metric tons, coal-tar colors.
12,360 metric tons, aniline oil and salts.

In this latter class the exports of 1898 were nineteen times as much as in 1883.

H. W. JAYNE.

## NOTE.

*Qualitative Tests for Boracic Acid.*—It seems not to have occurred to authorities on the subject to test the effect of the alcoholic vapors of boracic acid on turmeric paper. We find that, if the test is applied in the following manner, the presence of boracic acid in minerals is rendered more certain and delicate.

Use a test-tube about 2.5 cm. in diameter and 20 cm. long. Put into the tube about 0.1 gram of the substance, 0.5 cc. hydrochloric acid, and 10 cc. wood alcohol. Boil vigorously down to small bulk, agitating the lower end of the tube in flame of burner, and holding the moistened end of a piece of turmeric paper just outside the mouth, so as to catch the vapors. Boracic acid will finally color the turmeric a characteristic red. Now, if the turmeric is placed vertically on the side of a beaker so as to dip into a little distilled water to which a few drops of ammonia have been added, a pinkish to deep purple or blue will be produced, in marked contrast to the red produced by the ammonia on the end of the paper unaffected by the vapors.

LOS ANGELES, CAL.,
July 2, 1900.

E. M. WADE AND M. L. WADE.

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## NEW BOOKS.

THE CALCULATIONS OF ANALYTICAL CHEMISTRY. BY EDMUND H. MILLER, Ph.D. New York: The Macmillan Co. 1900. viii + 183 pp.

In nearly all of the books published on the calculations of analytical chemistry there is a distinct statement in the preface that the book has been published with the idea of preparing the student to pass certain examinations. This pernicious system, fortunately, has not invaded the American text-book to anything like the same extent as it has the English books of the same class. There has been in the past scarcely any attempt to lay down general principles in regard to chemical calculations. This book is a decided advance in an attempt to treat the subject from a broad point of view. Just how far it will succeed remains to be seen, for there are hardly any two teachers who will treat the subject in the same way. All will, I believe, agree that it is a distinct advance to present such a subject entirely free from formulas. The student is asked to solve the problems, applying his general knowledge of chemistry. If he has been successful

in applying and understanding the laws, he can then construct his formulas if he so wishes.

The book consists of ten chapters divided as follows: calculations of chemical equivalents and atomic weights; formulae and percentage; mixtures having a common constituent; equations; use of factors; volumetric analysis; density of solids and liquids; gases; calorific power; electric and electrolytic calculations for direct currents. In addition there is a series of tables of weights, measures, specific gravities, factors, logarithms, etc., which will be found useful to any one having occasion to make any calculations. There will, probably, be a greater difference of opinion over the chapter on normal solutions than over any other. The author's development of the subject is satisfactory, but he has not exhausted the possibilities for clear treatment of a subject which can be made particularly attractive and instructive. The book, if used in connection with classroom work, will undoubtedly be of great value, and should help the student to a much clearer understanding of the quantitative values of chemical laws. HENRY FAY.

COLOUR: A HANDBOOK OF THE THEORY OF COLOUR. BY GEORGE H. HURST. New York: D. Van Nostrand Co. 1900. Price, $2.50.

The author of this book of 158 pages is a member of the Society of Chemical Industry, and is already known by his works on soaps, lubricating oils, painters' colors, and a "Dictionary of Coal Tar Colours." In this handsomely printed volume he endeavors to present to those familiar with the practical printing and dyeing of textile fabrics, and the mixing of colors for artistic effects, the theory of color, its cause and production, together with some account of the instruments used by scientific men in the study and measurement of color. The opening chapter treats of the prismatic colors, the spectroscope, wave motion, phosphorescence, fluorescence, luminosity, and so forth, in the compass of 31 pages. Other chapters deal with the theories of color as propounded by Young, Helmholtz, Brewster, and Maxwell, with the physiology of light, with contrast, and with the application of color to decoration and design. In his preface Mr. Hurst acknowledges his indebtedness to the manuals of Chevreul, Benson, Rood, and Church.

The book is illustrated freely, containing no less than 72 cuts and 10 full-page colored plates; unfortunately for readers the plates, many of which contain several figures, are simply numbered and bear no references to the pages on which the text occurs that explains the figures, or that the figures illustrate. The figures on plate IV refer to texts on pages 79, 105, 106, and 114, and yet the plate faces page 48, and no indication is given of these references. It is true that the plates should be regarded as illustrating the text, but if the latter is first examined it will be found that references are not much clearer; on page 63 a reference to "Fig. 2, Plate 3" should read "Plate II., Fig. 2," and that to "Fig. 3" of the same plate should read "Fig. 4." Throughout the book, the plates bearing Roman numerals are referred to by Arabic figures, and lack of uniformity in the sequence of "Plate" and "Fig." increases the confusion. This unhappy blemish prevents easy study of the brilliant plates, but can be corrected in a second edition. There is an index and the volume is well bound. H. CARRINGTON BOLTON.

A POCKET BOOK FOR CHEMISTS. BY THOMAS BAYLEY. New York: Spon & Chamberlain; London: E. & F. N. Spon, Ltd. Seventh edition. xii + 559 pp. Price, $2.00.

This book is already well known to chemists. The new edition, according to the preface, has been "rearranged and to a large extent rewritten." In spite of this much is yet to be desired in the arrangement of the tables and many of them might be presented in a much simpler and more compact form. In the selection of matter, it seems to the reviewer, that the author has attempted to cover too much ground and that many of the tables are so seldom used and are so readily accessible to any one having occasion to use them that they could well be cut out, while others such as those under the sections X, alcohol, XI, beer, and XII, sugar, might well be left for the special pocket-books gotten out for these industries. Of course there is no objection to the insertion of these tables except that they add to the size of the book and make the useful tables less readily turned to. In spite of these defects the book contains much valuable information and many tables in every-day use by chemists.

RICHARD K. MEADE.

FIELD TESTING FOR GOLD AND SILVER. A Practical Manual for Prospectors and Miners. By W. HAMILTON MERRITT. London: Crosby & Lockwood; New York: D. Van Nostrand Co. 16mo. x + 144 pp. Illustrated. Price, $1.50.

This is a book for the prospector and contains full directions for such rough tests as can readily be used in the field. Part I (72 pp.) is devoted to assaying, Part II to practical mineralogy and geology, and Part III contains a glossary of useful mining terms and a list of common rock-forming minerals and rocks. The booklet is bound in flexible leather, and is of a size suitable for pocket use. E. H.

THE MANUFACTURE OF VARNISHES: OIL CRUSHING, REFINING AND BOILING. From the French of Ach. Livache, extended and adapted to English practice by John Geddes McIntosh. London: Scott, Greenwood & Co. 1899.

This book contains some information about raw materials which may interest the novice, nearly half the space being devoted to this, the greater part of which is reasonably correct. The author has collected a good deal of somewhat antiquated chemical literature on resins, the value of which is well indicated by the luminous observation on p. 18 that "The data are of no value, except in regard to the variety of copal which is referred to; and this is exactly the point which the investigators have almost invariably omitted to supply;" and "of little or no value to the practical varnish maker." The book is equally remarkable for what it contains and what it leaves out. For example, no reference is made to the almost universal practice of hardening rosin with lime; and it would be hard to compress more ignorance of the facts and of modern literature on asphaltums into a sentence than the following: "In its composition this mineral (Manjak) is similar to the pitch of Trinidad, to the gilsonite of Utah and the Canadian albertite." Nothing is said about oil-soluble aniline colors, but the incorrect statement is made that indigo-carmine is soluble in oil (p. 86). The present reviewer is not competent to criticize the chapter on spirit varnishes, except on one or two points. Shellac varnish is said to be made by dissolving one part of shellac in 5 to 12 parts of alcohol; such a solution can not be sold in this country, and probably not in England; regular shellac varnish is made with

5 pounds of shellac to 6½ pounds of alcohol. Much is said about wax in shellac but none of the practical modern methods of removing it are given. A brief and valueless section is given to the important subject of asphaltum varnishes. The preparation of raw linseed oil is well described; but a lot of venerable and worthless recipes for bleaching it are given, reference being sometimes made to "water-white" or "colorless" oil, something never yet produced, even approximately. The author seems ignorant of modern methods of oil-treatment, the most recent one referred to being Hartley's, which had been known and abandoned in this country before Hartley patented it.

Aside from references to Mulder and Chevreul (not very new) the treatment of the subject of driers is unsatisfactory. The fact is that the essential thing is to get a certain amount of lead or manganese into the oil, it makes no difference whether we use oxides, borates, or anything else; the other factor is the temperature needed. Zinc and magnesia salts are of no value, and are long out of date. Contrary to the statement on pp. 263–4, this reviewer has made excellent driers of nickel and cobalt, but they are too costly.

The section on oil and resin varnishes is especially unsatisfactory. It seems as if the translator ought to have been able to get some valuable matter for this, since the English varnish-makers produce varnishes which are up to date and of great excellence; but such does not appear to have been the case. The curious statement is several times made that in melting resins it is better to work with small quantities, 3 to 5 pounds, because the discoloration, produced by contact with the metal of the melting-pot, is less. Both theory and practice ought to show that the larger the vessel and the amount of resin the smaller is the heating surface per pound of resin, and the less the discoloration. It is, therefore, possible to melt 125 pounds at a time, which is the common American practice, and make a paler product than can be made in the laboratory. Before the use of the thermometer in this work the varnish-maker had various tests of heat, such as dropping in a bit of onion peel, which would brown and shrivel, or a feather, which would curl up with the heat when the temperature had reached a certain

point; but this fried-onion and burnt-feather business has now gone out of practice, notwithstanding what is said about it in this treatise.

One of the chief authorities quoted is Violette. Now Violette worked about half a century ago, and if he ever knew anything about practical varnish-making, which is doubtful, his book is out of date; and this is the general verdict to be passed on this book. It is misleading to the student, and of no value to the varnish-maker. A. H. SABIN.

## BOOKS RECEIVED.

The Manufacture of Varnishes. Oil crushing, refining, and boiling, and kindred industries; describing the manufacture and chemical and physical properties of spirit varnishes and oil varnishes; raw materials; resin; solvents and colouring principles; drying oils, their extraction, properties, and applications; oil refining and boiling; the manufacture, employment, and testing of various varnishes. Translated from the French of Ach Livache, Ingenieur civil des mines. Greatly extended and adapted to English practice with numerous original recipes by John Geddes McIntosh. London: Scott, Greenwood & Co.; New York: D. Van Nostrand Co. 1899. vii + 403 pp. Price, $5.00.

Commercial Fertilizers. By J. H. Stewart and B. H. Hite.—Bulletins Nos. 63 and 65. Sugar Beet Investigations in 1899. By J. H. Stewart and B. H. Hite.—Bulletin No 64. West Virginia Agricultural Experiment Station, Morgantown, W. Va. 82 pp.

Field Testing for Gold and Silver. A Practical Manual for Prospectors and Miners. By W. Hamilton Merritt. London: Crosby & Lockwood. New York: D. Van Nostrand Co. 16 mo. x + 144 pp. Illustrated. Price, $1.50.

Charbon (Anthrax). Further investigations and suggestions, with summary and conclusions. Second series No. 60, Bulletin of the Agricultural Experiment Station of the Louisiana State University and A. & M. College, Baton Rouge, La. 28 pp.

Bulletin No. 57.—The Smuts of Illinois' Agricultural Plants. 72 pp. Bulletin No. 58.—Composition and Digestibility of Corn-fodder and Corn Stover. 10 pp. Bulletin No. 59.—Orchard Management. University of Illinois Agricultural Experiment Station, Urbana, Ill. 26 pp.

Gardening under Glass. Bulletin No. 170. The North Carolina College of Agriculture and Mechanic Arts, Agricultural Experiment Station, West Raleigh, N. C. 24 pp.

Proceedings of the Twenty-fourth Annual Meeting of the Pharmaceutical Association of the State of South Carolina, held in Charleston, S. C., May 17, 1900. 30. pp.

The Chemistry of the Metals. By J. H. Kastle, Lexington. 1900. vi + 198 pp. 8vo.

Annali del Laboratorio Chimico centrale delle Gabelle. Diretti dal Dr. Vittorio Villavecchia. Volume IV. Roma: Tipografia Elzeviriana di adelaide ved. Pateras. 1900. 528 pp.

The Apple Orchard.—Bulletin No. 49. Agricultural Experiment Station of the University of Missouri, Columbia, Mo. January, 1900. 21 pp.

An Outline of the Theory of Thermodynamics. By Edgar Buckingham, Ph.D. (Leipzig). New York: The Macmillan Co. 1900. xi + 205 pp. Price, $1.90.

L'Eau dans l'Industrie. Par H de la Coux. Paris: Vve Ch. Dudon, Éditeur. 1900. 496 pp. Price, 15 francs.

Inspection and Analysis of Foods.—Bulletin No. 86. 51 pp. Kentucky Forage Plants; analyses of Some Kentucky Grasses.—Bulletin No. 87. 68 pp. with 14 plates. Kentucky Agricultural Experiment Station of the State College of Kentucky, Lexington, Ky.

Essentials of Medical and Clinical Chemistry, with Laboratory Exercises. By Samuel E. Woody, A.M., M.D. Fourth edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1900. viii + 243 pp.

An Ephemeris of Materia Medica, Pharmacy, Therapeutics, and Collateral Information. July, 1900. On Acetic Acid as a Substitute for Alcohol in Extracting the Active Principles of Some Officinal Drugs. By Edward R. Squibb, M.D. 10 pp.

Corn Culture in North Carolina.—Bulletin No. 171. The North Carolina College of Agriculture and Mechanic Arts, West Raleigh, N. C. May, 1900. 20 pp.

Twenty-third Annual Report of the Connecticut Agricultural Experiment Station for 1899. Part III.—Papers on availability of Nitrogen, fertilizers for forcing-houses, insect notes, on tobacco diseases and remedies, fertilization of melons, notes on Fungi, tobacco experiments, and vegetable proteids. New Haven, Conn. 1900. viii + 195 pp.

(1) H. R. 11350. A BILL to establish the National Standardizing Bureau. (2) Document No. 625, Letter from the Secretary of the Treasury, transmitting, with accompanying communications, a draft of a bill for the establishment of a National Standardizing Bureau. (3) Hearing before the committee on coinage, weights, and measures, House of Representatives, May 3, 1900. Superintendent of Document Room, House of Representatives, Washington, D. C.